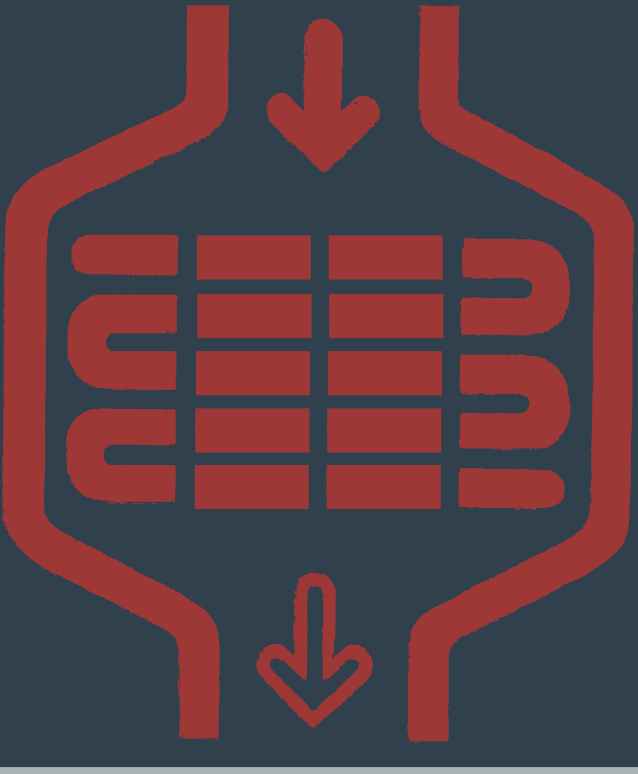
I. FURMER, V. ZAITSEV

General Chemical Engineering



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GENERAL CHEMICAL ENGINEERING

И. Э. Фурмер, В. Н. Зайцев

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I. E. FURMER AND V. N. ZAITSEV

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INTRODUCTION

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"Chemistry is broadly expanding its impact on human life. Its achievements can be observed everywhere." These words were spoken by the Russian scientist M. Lomonosov more than two hundred years ago. In modern times, they have proven even more justifiable than at the time of M. Lomonosov, since in recent years chemistry has penetrated into all spheres of industry, agriculture and daily life.

Plastics, rubbers, paint and varnish coatings have been widely employed in the engineering industry. Engineering achievements would have been impossible without the artificial materials supplied by the chemical industry. Chemical materials have been introduced into the construction industry, which had previously not used synthetic materials.

Chemical products are of great importance for the intensification of agriculture. Fertilizers give nutrients to plants, and pesticides protect plants against pests and diseases.

Fabrics, clothes, footwear, knitwear, artificial furs, leather, domestic appliances, and household articles are all provided by the chemical industry.

Public health uses chemical products, such as drugs, vitamins, and surgical materials, which are powerful helps in the struggle for human health.

Chemistry has been so widely and fruitfully introduced into other industries that a modern economy cannot rapidly develop without growth in the chemical industry.

Engineering is a science on methods and facilities for mass-scale processing of raw materials in consumer goods and means of production.

There exist manufacturing and chemical engineering.

Manufacturing engineering examines processes such as the processing of raw materials that do not generally bring about any change in the composition or the internal structure of the starting substance. For example, furniture is made from wood, machines and equipment are manufactured from metals, yarn and then fabrics are produced from cotton, flax, and wool.

Chemical engineering envisages chemical processing of raw materials when the composition, structure, and properties of the products obtained are not identical with those of the starting materials. For example, as a result of chemical processing, plastics, synthetic rubbers and synthetic fibres are manufactured from natural gas; fibres, acetic acid, and methanol, from wood; dyes, pharmaceuticals, and other products, from coal.

In a number of cases it is difficult to define the borderline between manufacturing and chemical engineering, since a change in the shape and external appearance of materials may sometimes be accompanied by chemical reactions. And, vice versa, chemical processes that bring about a change in the composition of substances are accompanied by mechanical processes.

Modern chemical enterprises are industrial complexes at which complex processes are being carried out. High-skilled workers are required to run them.

At the present time, there are tens of thousands of products manufactured by chemical and related industries. It is not feasible to acquaint students with the manufacture of each product. It is essential therefore that every student should be provided with information on the regularities inherent in chemical processes and on the use of these regularities to apply these processes in practice.

Due to this fact, the course in general chemical engineering is acquiring a special importance in the training of industrial workers. The authors of this book deal with the theoretical fundamentals of chemical processes in a form comprehensible to students of vocational training schools, and show their application by giving specific examples in the manufacture of major chemical products.

Chapter 1

TECHNICAL AND ECONOMIC INDICES OF CHEMICAL TECHNOLOGICAL PROCESSES

The purpose of chemical engineering is to carry out processes as advantageously as possible, to transform raw materials into reaction products as fully as possible, to obtain the maximum amount of a product from the given raw material, and to increase the product output in a reactor per time unit, i.e. to enhance the processing rate of the raw material. In this case, attempts are made to obtain a high-quality product and to minimize all the expenses involved in its production.

There are *technical and economic indices* to analyze a process and determine its efficiency.

In order to define a process, it is essential to know to what extent the raw material is utilized and how completely its chemical transformation occurs. This can be established by comparing the final amount of the reactant with its initial amount. For example, a simple irreversible reaction occurs, such as:

$$A \rightarrow B \tag{1.1}$$

Let us assume that G_{A_0} is the initial amount of reactant A (at the beginning of the process), and G_A is the amount of reactant A on completion of the process. It is necessary to establish the extent to which reactant A has undergone a chemical transformation. To this end, the amount of reactant A consumed in the reaction, $G_{A_0} - G_A$, is related to its initial amount, G_{A_0}. The resultant value is the fraction of reactant A which has undergone chemical transformation. This value is designated as x_A and is called **the degree of conversion:**

$$x_A = \frac{G_{A_0} - G_A}{G_{A_0}} \tag{1.2}$$

Thus, *the degree of conversion is the ratio of the amount of the reactant consumed in the reaction to its initial amount.*

The higher the degree of conversion x_A, the greater the amount of the initial material that is reacted, and the more complete the chemical transformation process.

The efficiency of the process is also determined by another index, the **product yield**. *The product yield is the ratio of the amount of the resulting product to the maximum obtainable amount.* For the reaction A → B, the yield Φ_B is equal to:

$$\Phi_B = \frac{G_B}{G_{B\,\max}} = \frac{G_B}{G_{A_0}} \qquad (1.3)$$

where G_B is the amount of substance B which is actually obtained and $G_{B\,\max}$ is the maximum amount of substance B obtainable from a given process.

The maximum amount of a product yielded from a given amount of raw material is calculated by the reaction equation. Here, the content of the reactant in the raw material to be transformed should be taken into account. This can be demonstrated using an example illustrating lime (CaO) production by decomposition of calcium carbonate ($CaCO_3$) contained in limestone according to the reaction:

$$CaCO_3 = CaO + CO_2 \qquad (1.4)$$

We must determine the maximum amount of CaO that can be derived from 100 kg of limestone which consists of 90 per cent $CaCO_3$.

First, the amount of calcium carbonate contained in 100 kg of limestone is calculated:

$$\frac{100 \times 90}{100} = 90 \text{ kg}$$

Next, the amount of CaO that can be produced from 90 kg of $CaCO_3$ is determined from the reaction equation:

$$\frac{90 \times 56}{100} = 50.4 \text{ kg}$$

where 100 and 56 are the molecular weights of $CaCO_3$ and CaO, respectively.

Thus, as much as 50.4 kg of CaO can be obtained from 100 kg of limestone.

In complex reactions, when the same starting material may undergo various chemical transformations to yield different reaction products, it is not sufficient to evaluate the course of the process only in terms of the degree of conversion. The degree of conversion may be high, i.e. the greater part of the starting products are reacted, but this conversion will not always lead to the formation of the desired (final) products. In addition to the desired products, some undesirable by-products may be formed. The more desired products and the less by-products are formed, the more efficiently the process occurs. **Selectivity** is the quantity used to characterize such complex processes and to determine the proportions of the desired products in the total amount of the resulting products.

Selectivity is the ratio of the amount of the desired product to the total amount of the resulting products.

For instance, if the process involves concurrent reactions:

$$A \rightarrow B, \quad A \rightarrow D \tag{1.5}$$

where B is the desired product and D is the by-product whose amounts are represented by G_B and G_D, respectively, the selectivity φ_B is equal to:

$$\varphi_B = \frac{G_B}{G_B + G_D} \tag{1.6}$$

Since the total amount of the resulting products is equal to the amount of the substance A consumed in the reaction

$$G_B + G_D = G_{A_0} + G_A \tag{1.7}$$

selectivity may be defined as the *ratio of the amount of the resulting desired product* B *to the amount of the converted reactant* A:

$$\varphi_B = \frac{G_B}{G_{A_0} - G_A} \tag{1.8}$$

Below is an example that demonstrates how the degree of conversion, yield, and selectivity are calculated for a process that involves a complex reaction.

Example. To obtain formaldehyde (HCHO), methanol (CH_3OH) is oxidized using a silver catalyst:

$$CH_3OH + 0.5O_2 = HCHO + H_2O \tag{1.9}$$

In addition to this main reaction, some concurrent reactions occur that produce formic acid (HCOOH), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), and other products.

Let us assume that 3.2 kmoles of methanol were used for oxidation purposes. A total of 1.8 kmoles of formaldehyde and 0.8 kmole of by-products were produced from that amount, and 0.6 kmole of methanol remained unoxidized. The degree of conversion of methanol x_{CH_3OH}, the formaldehyde yield Φ_{HCHO}, and the process selectivity with respect to formaldehyde φ_{HCHO} are to be determined.

Solution. 1. *The degree of conversion.* To determine the amount of the alcohol consumed, the 0.6 kmole that remained after the reaction should be subtracted from its starting amount of 3.2 kmoles. Then:

$$x_{CH_3OH} = \frac{G_{(CH_3OH)_0} - G_{CH_3OH}}{G_{(CH_3OH)_0}} = \frac{3.2-0.6}{3.2} = 0.81$$

2. *The yield of formaldehyde.* A maximum amount of formaldehyde will be obtained if all of the methanol is transformed into HCHO. It follows from Eq. (1.9) that one molecule of the alcohol yields one molecule of the formaldehyde and the maximum possible amount of formaldehyde will therefore be $G_{HCHO_{max}} = 3.2$ kmoles. 1.8 kmoles were actually obtained. Then:

$$\Phi_{HCHO} = \frac{G_{HCHO}}{G_{HCHO_{max}}} = \frac{1.8}{3.2} = 0.56$$

3. *Formaldehyde selectivity.* The total amount of the resulting products is equal to the sum of the amount of the formaldehyde ($G_{HCHO} = 1.8$ kmoles) and the by-products ($G_{b\text{-}pr.} = 0.8$ kmole). Therefore:

$$\Phi_{HCHO} = \frac{G_{HCHO}}{G_{HCHO} + G_{b\text{-}pr.}} = \frac{1.8}{1.8+0.8} = 0.69$$

In addition to the degree of conversion, yield, and selectivity,there are some other values used to define a process.

Capacity is the amount of the product or the processed raw material produced per time unit. It indicates the efficiency of the performance of machines, equipment shops, and factories. Capacity is measured in kilograms per hour (kg/h), in tons daily (t/daily) or in cubic metres daily (m^3/daily). The maximum obtainable capacity is called **power**. Power is measured in the same units as capacity.

Intensity indicates the performance of equipment or installations in which the same chemical processes occur. Intensity is the capacity related to some quantity that specifies the size of an apparatus (its volume or cross section). Intensity may be measured, for example, by the amount of kilograms of the product obtained per hour from the unit of the apparatus volume ($kg/h \cdot m^3$), or by the amount of tons of the product obtained daily from the unit apparatus cross section ($t/daily \cdot m^2$).

However, for a full definition of the process, the indices listed above are not sufficient. A chemical-technological process is considered complete if it is also economically efficient. The economic efficiency of production is evaluated according to several indices, **the product cost** being the most important.

Manufacturing costs are the expenses borne by the enterprise in monetary terms; they are directly related to the manufacture of a given product. The sums spent in manufacturing a product and expenses involved in its sale are called **the full product cost.**

The following illustration shows what basic expense items comprise the manufacturing costs of a product:

1. To manufacture a product, certain raw materials are essential. Therefore, the first expense is **the cost of the raw and basic materials** directly involved in the chemical production processes.

2. A certain quantity of energy is required to transform a raw material into a product. **Fuel and energy** for technological purposes are the second item of expenses included in the product cost.

3. To effect chemical transformations, space and equipment are required. Certain means are spent to construct industrial buildings and installations and to furnish them with equipment (fixed productive assets). As a result of use, the productive assets gradually depreciate. Their deprecia-

tion is compensated by the gradual transfer of their cost to the product being manufactured over the course of the service life of the fixed productive assets. Compensation for the depreciation of these assets is called **depreciation charges (depreciation)**. This is the third expense in the product manufacture.

4. The product cost also includes **wages of workers** who are involved in the basic production processes, i.e. workers who directly attend to chemical equipment.

5. The next expense is the **departmental charges**. These are expenses that reflect the maintenance of the fixed productive assets (including wages of workers in auxiliary and repair services, also the wages of shop management personnel, and expenses for labour protection and industrial safety measures).

6. **General plant expenses** are expenditures for the repair of buildings, and also administrative expenses.

The value of the by-products obtained from the same raw material is generally subtracted from the production cost of the basic product. The proportion of expenses to the cost of various production items is different for individual chemical industries. However, in most cases, the basic expenses are for raw materials; they average 60 to 70 per cent for the chemical industry, and about 10 per cent for fuel and energy. Wages in the production cost of chemical products are 4 per cent, and amortization, 3 to 4 per cent.

It is obvious from these data that the product cost in the chemical industry depends primarily on the cost and the effective use of raw materials and on the cost and consumption of fuel and energy. Hence, the economical utilization of raw materials, fuel, and energy is the basic precondition for reducing the product cost.

The amounts of raw materials and energy consumed for the manufacture of a unit of output are called **consumption factors**, which are expressed in terms of tons per ton (t/t) and cubic metres per ton (m^3/t) for raw materials, and kilowatt-hours per ton (kW·h/t) for energy, and so on.

For example, it is known that to produce 5 t of sulphuric acid, 4.5 t of a raw material (iron pyrite) are consumed. Then, the raw material consumption factor will be equal to $4.5:5 = 0.9$ t of iron pyrite per 1 t of sulphuric acid.

REVIEW QUESTIONS

1. What basic technical and economic indices are used to determine the efficiency of a technological process?
2. What quantity is used to define the extent of conversion of the starting materials?
3. Is it sufficient, in a complex reaction, to know only the degree of conversion of the starting reactant to judge whether the process is efficient?
4. What are the basic items which make up the production cost of chemical products?

Chapter 2

RAW MATERIALS AND ENERGY FOR THE CHEMICAL INDUSTRY

2.1 Raw Materials for the Chemical Industry

Raw materials are naturally occurring materials employed in the manufacture of industrial products. **Intermediate products** are materials that result from the industrial processing of raw materials at a given enterprise and are employed as starting materials for the manufacture of a product. **Waste products** are by-products that are not used at a given enterprise, but can serve as the raw material for the manufacture of some chemical products.

Raw materials are an indispensable element of any chemical technological process, which determines, in many respects, its technological and economic aspects.

The environment serves as an inexhaustible store from which the chemical industry obtains its raw materials. As science and technology make progress, new mineral resources are being used for manufacturing chemical products, new types of raw materials are being developed, and the industrial raw materials base is being expanded.

A great variety of raw materials are processed at chemical plants. The chemical industry uses common salt crystals in the manufacture of artificial leather and knitted linen, pharmaceuticals, and electroinsulating materials. Components of the most complex machines, dyes, and consumer goods are manufactured from coal by chemists. Elastic rubber, solid plastics, tough and beautiful fibre, fertilizers, varnishes, solvents, drugs, and detergents are just a few of the products derived from petroleum and natural gases. Light grey stone—apatite ore—called "the stone of fertility" is used for the manufacture of fertilizers. In addition to fertilizers, aluminium for the aircraft industry, soda, and cement for construction can be derived from this ore. Chemists skilfully transform sand into glass, cement, lubricants and films that withstand high temperature, and air is transformed into fertilizers, knitted fabrics, and dyes.

Types of Raw Materials. It is difficult to itemize all the raw materials that are processed at chemical plants. However, in spite of their great variety, raw materials in the chemical industry may be classified by their *origin* as mineral, plant, and animal, or by the *state of aggregation*, into solid, liquid, and gaseous, or by their *composition* as inorganic and organic substances.

Mineral raw materials are those resources that are mined from the earth which can, at a given level of technology, be utilized advantageously by the national economy. Mineral raw materials are generally subdivided into three types: ore-bearing, non-metallic, and fuel raw materials.

Rocks from which metals can be extracted and used to economic advantage are called *ore-bearing raw materials.* In addition to metals, chemical products can also be manufactured when processing some types of ore-bearing raw materials. For example, in addition to copper, zinc, and nickel, sulphuric acid can also be produced.

Non-metallic raw materials are rocks employed in the manufacture of chemical, building, and other non-metallic products. They are not a source for metal extraction. Raw materials that contain sulphur, phosphorites, apatites, potassium salts, common salt, sand, gravel, clays, etc. are included in this type of raw material. The latter serve as a source in the manufacture of various chemical products. Some examples on the use of non-metallic raw minerals are presented in Diagrams 1 and 2.

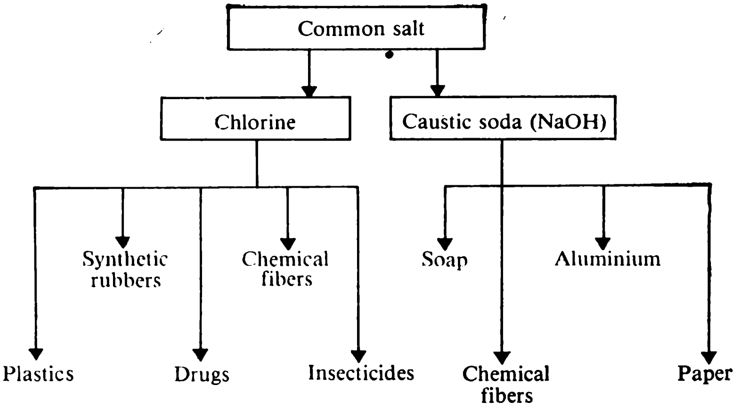


Diagram 1. Use of common salt

Combustible mineral raw materials include coals, petroleum, peat, oil shales, and natural gas. Chemists can derive a great variety of chemical products from combustible raw materials. Diagrams 3, 4, 5, and 6 present a few examples of this type of raw material. It is apparent from these diagrams that petroleum, coal, and gas are useful for chemists not

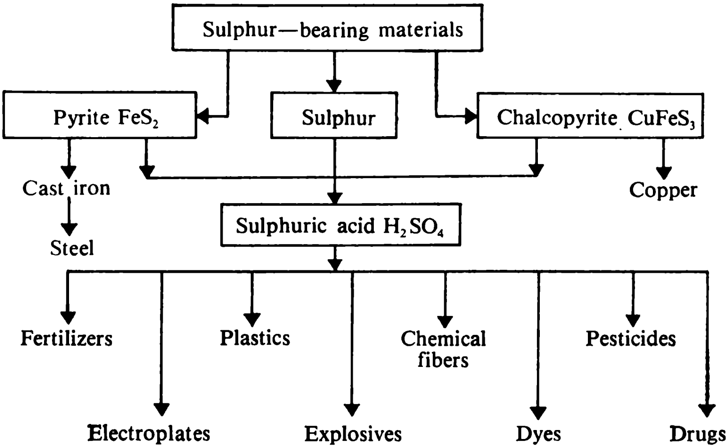


Diagram 2. Utilization of sulphur-containing raw material

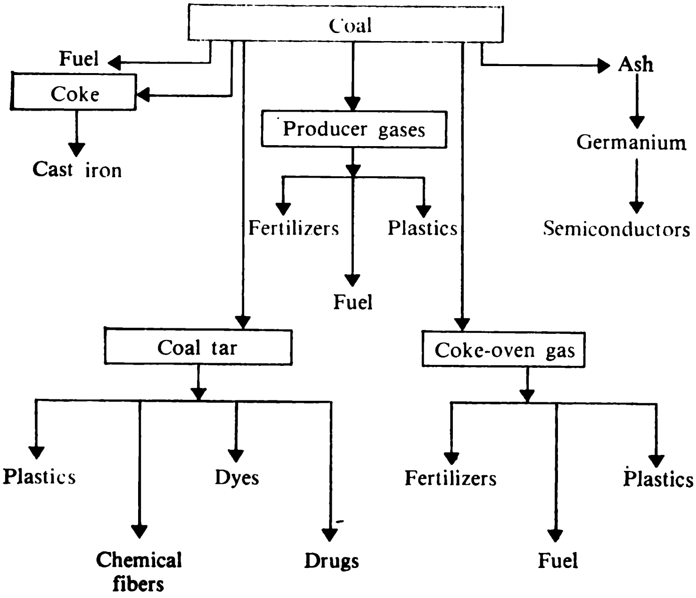


Diagram 3. Coal utilization

only to generate heat but also as sources of immense material value.

Various coals produce dyes, drugs, and beautiful, delicate articles from chemical fibres, as well as diverse articles from plastics, semiconductor materials for transistor radio sets, TV sets, and fertilizers.

Petroleum is one of the most valuable substances that nature has given to us. It is difficult now to imagine our life without airplanes, cars, tractors, and combines. The fuel for all of these is derived from petroleum. Petroleum is also a raw material for manufacturing fibres, synthetic rubbers, plastics, and detergents. It is not an accident that petroleum is called "black gold". Fertilizers, plastics, varnishes, chemical fibres, etc. can be derived from natural gas.

Mineral raw materials are mined in various parts of the Soviet Union. Work by the Soviet scientists V. I. Vernadsky, N. S. Kurnakov, A. E. Fersman, I. M. Gubkin, and others contributed to the development of the fundamentals

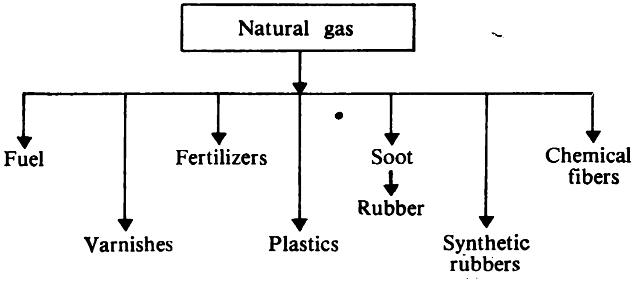


Diagram 4. Natural gas utilization

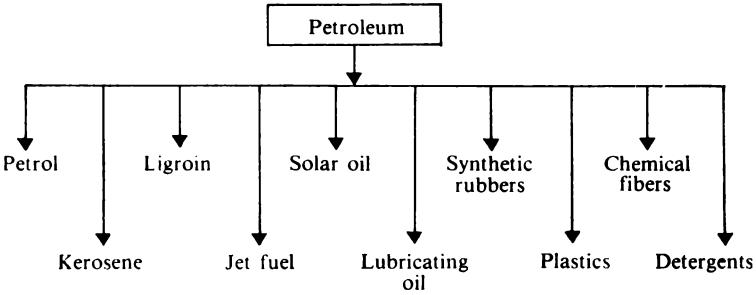


Diagram 5. Petroleum utilization

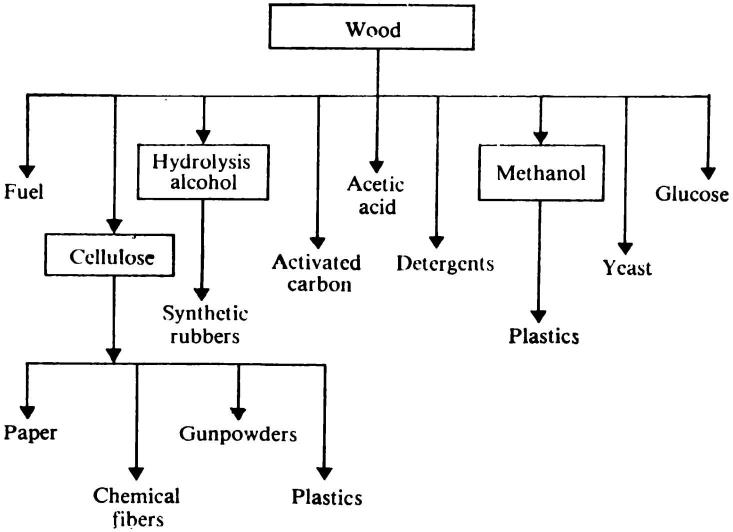


Diagram 6. Use of wood

of prospecting, mining, and processing of raw materials of various types.

Currently, the Soviet Union is number one in the world in reserves prospected of phosphorites, apatites, potassium salts, common salt, and other types of raw materials.

Plant and animal raw materials are subdivided according to their use into edible and inedible types. *Edible raw materials* include agriculture, forestry, and fishery products used as foodstuffs (potatoes, sugar beet, cereals, edible fat, etc.). The chemical and other industries employ inedible plant and animal raw materials that can be processed into products or materials intended for domestic or industrial purposes. This type of raw material includes cotton, wood, straw, flax, hemp, skin, wool, fur, whale and cod liver oil, and animal bones. Wood is an example of the use of a plant raw material (see Diagram 6).

In addition to mineral, plant, and animal raw materials, air and water serve as raw materials for the chemical industry.

Air is practically an inexhaustible raw material. Air is composed predominantly of nitrogen (about 78 per cent), about 21 per cent oxygen, and the rest are noble gases (argon, neon, krypton, and helium). All the constituents of air have found application in the national economy. As can be seen in Diagram 7, a great variety of products and materials, ranging from drugs manufactured in amounts calculated in grams and kilograms to millions of tons of fertilizers, can be obtained from air.

Water serves not only as a source of hydrogen and oxygen, but it is also involved in many chemical processes entering into various chemical reactions. For example, water can be used to produce sulphuric, nitric, and other acids, alkalis, and so on. In a number of cases, water is used for dissolving solid, liquid, and gaseous substances. Water is also used for heating and cooling the reactants at chemical plants.

Water is consumed in immense quantities by chemical plants, measured in millions of cubic metres daily at large integrated enterprises.

The Use of Raw Materials. Chemical raw materials are rather diversified, and their reserves are huge. At the same time, the occurrence of individual elements in the Earth's crust is exceedingly irregular. About half the weight of the Earth's crust is made up of oxygen, 26 per cent silicon, followed by aluminium (7.45 per cent), and iron (4.2 per cent) in terms of their occurrence. Nine elements (oxygen, silicon, aluminium, iron, calcium, sodium, magnesium, potassium, and hydrogen) constitute about 98 per cent of the weight of the Earth's crust, and all the other elements only 1.9 per cent. Carbon, life's major element, constitutes as little as 0.35 per cent of the Earth's crust, and 76 elements, including widely used lead, mercury, and arsenic, constitute 0.06 per cent. Hence, it follows that our usual concepts of the occurrence of individual elements do not correspond to reality.

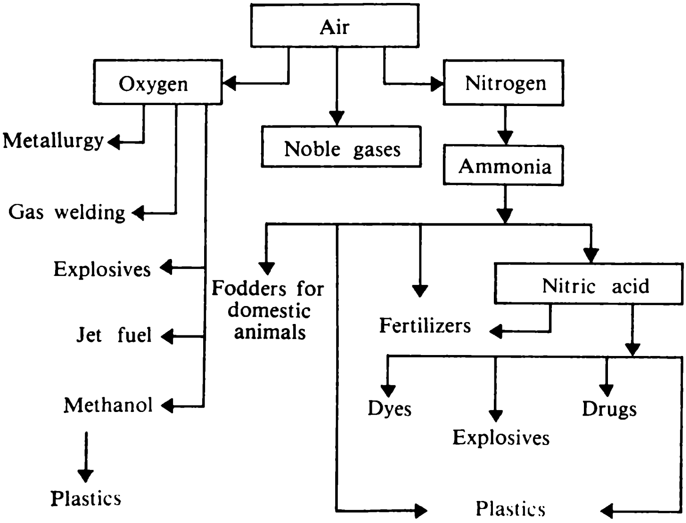


Diagram 7. Air utilization

The Soviet Union's chemical industry currently uses more than 80 elements. It is apparent from the above that deposits of some elements are not great and therefore the difference between the reserves and the consumption of some elements is a problem that needs careful and rational utilization of raw materials. The Soviet Union has taken upon itself the following basic tasks in order to utilize rationally raw materials: the search for and uses of cheap raw materials, the integral utilization of raw materials, the recovery of raw materials, the reuse of waste products, the uses of concentrated raw materials, and the replacement of edible by inedible raw materials.

Search for and uses of cheap raw materials. Raw materials should predominantly be utilized locally, i.e. the raw materials where they are found should be consumed so as to require no further transport. In a number of cases, another industrial waste product is used as a raw material in the manufacture of one of the products.

The use of easily mined and cheap raw materials is an indication that the technological processes are economically efficient. For example, it has been long thought that the basic fuel and raw material for the Soviet Union's chemical industry is coal. However, it is more convenient and cheaper to pipe petroleum and gas than to carry coal by rail. Petroleum and gases burn down, whereas the combustion of coal gives huge amounts of ash (slag) and during the combustion of petroleum and gases, heat evolution is greater than during the combustion of coal. However, this does not mean that coal is being replaced by petroleum and gas in chemical processing.

The type of fuel used in the manufacture of chemical products should be decided according to the needs of each individual production process.

It should be taken into account that as petroleum and gas reserves are being gradually depleted, the value of these raw materials is increasing and they are being replaced by coal.

Industrial waste products may prove to be a cheap raw material. Currently, as engineering and technology are making progress, yesterday's waste products often become valuable industrial raw materials.

Integral utilization of raw materials. This task requires that all the basic components of raw materials are used effectively in the manufacture of various products and materials. The integral utilization of raw materials produces no industrial waste products, i.e. everything that is contained in raw materials is being utilized.

Petroleum refining, processing of coal, natural gas, common salt, sulphur-bearing ores, phosphites and apatites, and wood are examples of the integral utilization of raw materials (see Diagrams 1-7). The examples given in these diagrams do not exhaust the possibilities of integral processing of raw materials. They merely show that many products can be obtained from one type of raw material, which undoubtedly results in manufacturing cheaper products.

The integral utilization of raw materials is of great importance, since it reduces the consumption of raw materials. For example, the manufacture of fertilizers from natural gas makes it possible to manufacture simultaneously rubber, acetic acid, plastic materials, chemical fibres, and other products without additional consumption of raw materials. It is exceedingly important that integral processing of raw materials eliminates industrial waste products, many of which cause irreparable damage to the environment and human health.

Raw material recovery. The conversion of already reacted substances back to their original state for reuse is called raw material recovery. For example, reacting a solution of common salt with ammonia and carbon dioxide gives a sodium bicarbonate ($NaHCO_3$) precipitate, which is further employed in the production of soda and ammonium chloride (NH_4Cl) solution, reaction (2.1). Treatment of this solution with lime milk with heat according to reaction (2.2) produces ammonia, which is reused to carry out reaction (2.1)

$$NaCl + CO_2 + \overset{\downarrow}{NH_3} + H_2O = NaHCO_3\downarrow + NH_4Cl \qquad (2.1)$$

$$2NH_4Cl + Ca(OH)_2 = CaCl_2 + 2\boxed{NH_3} + 2H_2O \qquad (2.2)$$

Reaction (2.2) describes the process of ammonia recovery.

Utilization of waste products. Despite the fact that integral processing of raw materials is widely used, considerable amounts of waste products remain at some chemical enterprises which have not yet been consumed. They are discharged from these enterprises and generally pollute water reservoirs, contaminate the soil and air, and encumber the factory areas and those located closest to them. For example, soda-making plants produce large amounts of liquid waste products that contain dissolved salts (e.g. $CaCl_2$) and solid particles. So-called "white seas" are formed near soda-making plants in the pits into which these solutions are discharged. The "seas" contaminate the area, and the solutions they contain are absorbed by the soil rendering it dead.

The Soviet Union has established standards for the permissible content of substances in industrial waste gases and waste waters. Special purification installations are being constructed at chemical enterprises to render waste products harmless. The chemists' problem is not only to render waste products harmless, but also to create waste-free production cycles which use waste products to manufacture products essential for the national economy. Development of these processes is inseparably linked with integral utilization of raw materials.

The use of concentrated raw materials. Attempts should be made to use raw materials that contain certain substances in a very high concentration. Using such raw materials makes their processing cheaper and simpler, and also allows obtaining high-quality products. Unfortunately, the raw materials consumed by the chemical industry are not always concentrated and, therefore, prior to being processed, they are "beneficiated" either at concentrating mills or when extracting products from raw materials.

Replacement of edible raw materials by inedible ones. Many chemical products and materials have, up to the present time, been derived from edible raw materials. For this purpose millions of tons of grain, potatoes, vegetable oil, and animal fats were consumed. For example, ethanol is essential in the manufacture of synthetic rubber. About 10 or 11 t of potatoes or 4 t of grain must be processed to produce 1 t of ethanol.

This example shows how the chemical industry consumes huge amounts of foodstuffs. In view of this, it is clear how important, how essential it is to replace foodstuffs by inedible products in the chemical and other industries. Products obtained from inedible raw materials cost less than those obtained from edible. Plant and animal edible raw materials have largely been replaced by synthetic ones in the manufacture of rubber, dyes, varnishes, drugs, many plastic materials, and other materials.

The problem now before us is how to obtain basic foodstuffs, such as starch and sugar, from inedible raw materials, and also how to obtain artificially the constituents of protein, the source of life.

2.2 Preparation of Raw Materials for Processing

One of the major techniques for preparing raw materials for processing is their beneficiation.

Beneficiation is the treatment of raw materials with a view to separating the valuable constituent from the worthless portion, the gangue and, when required, to separate individual substances. Instead of raw materials containing minor amounts of useful substances, beneficiation produces concentrated raw materials.

The use of concentrated raw materials makes their processing more efficient, for the higher the concentration of a raw material valuable constituent the higher the rate of its chemical transformation, the simpler it is to process it, and the lower its energy consumption. Besides, beneficiation of raw materials where they are mined saves the user, transportation charges, because the beneficiated raw materials contain much smaller amounts of undesirable (unusable) constituents than those in unbeneficiated raw materials. And, finally, beneficiation allows the industrial processing of raw materials that have a low content of a valuable constituent; if these raw materials are not concentrated, they prove to be unusable. This is especially important when one remembers that the reserves of concentrated raw materials in nature are being gradually depleted. These circumstances require the wide use of beneficiated raw materials in the Soviet Union, and the construction of concentrating mills where the raw materials are being mined.

Solid materials such as various rocks, liquid materials such as solutions, and also gases are subjected to beneficiation, accomplished via various methods. All these methods are based on a difference in the physical, chemical, or physicochemical properties of the constituents in the raw materials.

A solid material (for example, rock) enriched with a valuable constituent is called a **concentrate**, whereas waste products, which contain the gangue, are called **tailings**. A solid mineral raw material is generally not found in a pure form. Most frequently, it is composed of several minerals.

The valuable constituent and the gangue of raw materials differ in their physical, physicochemical, or chemical properties, namely, density, hardness, solubility, wettability with individual liquids, and melting points. A complex mineral raw material can be separated into concentrate and tailings because of a difference in these properties.

If the valuable mineral and the gangue in the raw material have differing strengths (hardness), different breaking (or loosening) power at impact, then the raw materials are preliminarily crushed. In this case, weaker minerals, which are included in the composition of the raw material are crushed into finer grains and crystals than stronger minerals. The crushed raw material is screened through sieves of various mesh size. Large lumps remain in the sieve, while smaller lumps pass through. Depending on the number of sieves and mesh size, the raw material may be divided into a number of portions (fractions). Each sieve retains particles of certain size and, hence, various hardness. Therefore, each sieve yields a fraction beneficiated by some mineral.

A difference in the rate at which the particles fall is used to enrich raw materials, depending on their density and grain size in a stream of a liquid or gas. **The gravity concentration method** is based on this property. Figure 1 shows the diagram of wet gravity concentration when solid particles are settled in a stream of a liquid (most frequently, water). The crushed raw material in a tank that has a stirrer is mixed with water and is passed in pulp form (a suspension of the crushed solid material in liquid) through settling chambers (troughs) *I*, *II*, and *III* which have cone-shaped bottoms (bins) in succession. The largest and heaviest particles settle in a minimum period of time; therefore, they settle in chamber *I*. Average-sized fractions settle in chamber *II* and light (fine-grain) fractions settle in chamber *III*.

An apparatus having one, two, three or more chambers may be employed for separation purposes, depending on how many fractions the material should be divided into.

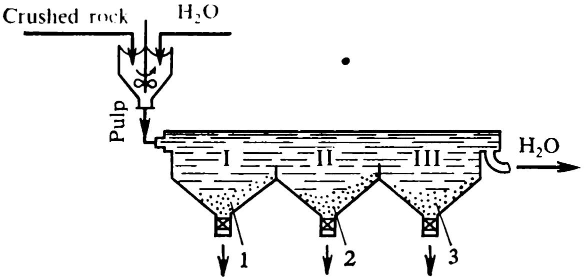


Fig. 1. Schematic diagram of wet gravity concentration
I, *II*, and *III*—settling chambers; *1*, *2*, and *3*—bins

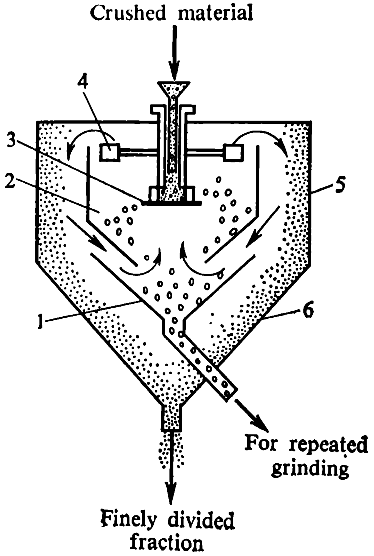


Fig. 2. Centrifugal air separator
1—internal cone; *2*—internal cylinder; *3*—plate; *4*—fan impeller; *5*—external cylinder; *6*—external cone

The fractions are withdrawn from bins *1*, *2*, and *3* through holes.

Dry gravity concentration is based on the same principle as wet concentration, but differs from the latter in that solid particles settle in a gas stream, rather than in a liquid stream. Figure 2 shows the diagram of a centrifugal air separator. It is essentially cylinder *5* provided with cone *6* (an external cylinder and a cone). The main cylinder concentrically mounts the second cylinder *2* with cone *1*. Plate *3* and fan impeller *4* are inserted in the internal cylinder through a separator cover. The plate and the fan impeller are rotated by an electric motor located above the separator cover. Rotation of the plate and the fan impeller inside the separator causes air currents to form (shown by arrows in the diagram). The crushed material fed to the plate during its rotation spills over the internal cylinder section. Fine particles are trapped by the air current created by the fan impeller and are brought into the space between the external and internal cylinders, where, striking against the walls (thus losing their velocity), the particles fall downwards and are withdrawn from external cone *6* as a finely divided fraction. Large particles overcome the resistance of the air current and fall downwards in internal cone *1* from which they are withdrawn.

Electromagnetic separation is employed when the raw material is composed of magnetosusceptible materials (capable of being attracted to a magnetic pole) and non-magnetic materials (which are not attracted to a magnet). Thus, magnetite and chrome iron ore (magnetic materials) may be separated from the gangue (non-magnetic portion of the raw material). Figure 3 shows the schematic diagram of an electromagnetic separator. The crushed material is fed into conveyer belt *1* which has drum *2* with electromagnet *3* installed inside. When the conveyer belt makes contact with the surface of the rotating drum particles of the material that are not magnetic are not attracted to the magnet and therefore are dumped from the belt into bin *4*. Magnetic particles are attracted by a magnet and adhere, as it were, to the belt surface. The particles continue moving until the belt passes through the magnetic force. Only after that are they broken off from the belt's surface and dumped into bin *5*.

Electrostatic separation is used to separate materials having different electric conductivity. Beneficiation is effected in a similar manner to the electromagnetic method. The difference is that, in an electrostatic separator, the drum has a negatively charged electrode instead of a magnet. Particles with high electric conductivity become negatively charged when they are subjected to a negatively charged electrode while the belt is moving. Therefore they are repelled from the belt and are dropped into a bin placed at some distance from the drum. The particles that possess no electric conductivity (dielectrics) are not capable of being charged from an electrode and therefore they are not repelled from the belt and are discharged into a bin located closer to the drum.

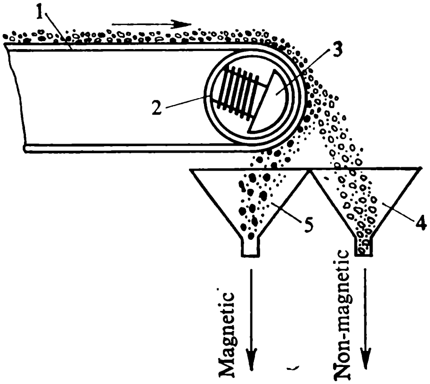


Fig. 3. Electromagnetic separator
1—conveyer; *2*—drum; *3*—electromagnet; *4* and *5*—bins

Iron and copper pyrites, lead glance, gold, and silver (substances having a good electrical conductance) can be separated from limestone, gypsum, and sand (substances that do not conduct current) by electrostatic separation.

The flotation method is widely employed for beneficiation of raw materials. It is based on the fact that grains of individual minerals have a different wettability with liquids (most frequently, with water). If finely divided particles of non-wettable (hydrophobic) mineral A and wettable (hydrophilic) mineral *B* are placed on the surface of a liquid, as shown in Fig. 4, the hydrophobic particle will be forced, as it were, out of the liquid, while being encircled with an air film, whereas the hydrophilic particle becomes rapidly enveloped with a liquid film. Therefore, if the raw material intended for flotation is first pulverized into dust, then made turbid in water so as to form a pulp or suspension, and finally fine air bubbles are passed through the suspension, the particles of minerals having a non-wettable surface will adhere to the air bubbles and will be carried by these bubbles (will float up) to form a froth on the surface of the water.

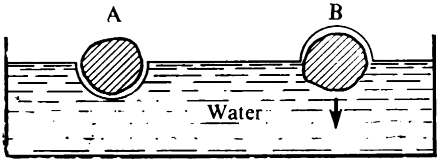


Fig. 4. Principle of separation of particles of non-wettable and wettable materials

A—non-wettable (hydrophobic) minerais, *B*—wettable (hydrophilic) minerals

Unlike the hydrophobic particles, the hydrophilic water-wettable particles can easily be enveloped in a liquid. Therefore they do not adhere to air bubbles and remain in a suspended state in the liquid. Over the course of time these particles settle to the bottom of a flotation apparatus.

In industry, a suspension of finely divided rock (grain size not exceeding 0.2 mm) is fed to a flotation machine. Two types of machines are employed, those using mechanical stirring of a pulp and simultaneous air feed, and those using air stirring. Figure 5 shows the cross-sectional view of a flotation machine using air to stir a pulp. The inside of a trough-shaped reservoir, chamber *1*, is provided with vertical partitions *2* between which tubes *3* are located. Air is fed under pressure along these tubes from collector *5* to chamber *1*. The air stirs the aqueous suspension, and air bubbles carry the hydrophobic mineral particles rising to the surface of the liquid. At the same time, the air makes the suspension circulate in the chamber (shown by arrows in the figure).

A small amount of **frother** is added to the suspension to retain the supernatant particles of the hydrophobic mineral on the surface of the liquid as much as possible. Frothers include pine oil, wood tar, and some fractions of coal tar pitch. The froth is composed of air bubbles, with mineral particles adhered to them, and is admitted from the surface of the liquid through the chamber side into chute *4* from which it is directed to vessels where it disintegrates (i.e. the bubbles burst). Non-wettable particles carried away by gas bubbles remain on the bottoms of the vessels. The resultant sediment of the mineral extracted from the ore in concentrated form is called a **flotation concentrate**. The hydrophilic mineral particles sink to the chamber bottom and are collected there in the form of a sediment called **flotation tailings**.

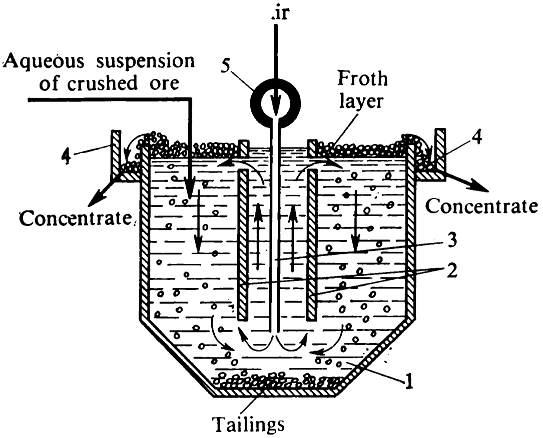


Fig. 5. Flotation machine using air agitation
1—chamber; *2*—partition; *3*—tube; *4*—chute; *5*—collector

Comparatively few natural minerals float naturally, i.e. have poor water wettability, like native sulphur, graphite, and ozocerite. Most minerals are water wettable, and special agents that reduce their wettability should be added to the suspension to separate them by flotation. These agents are known as **collectors**. Collectors may be oleic acid, naphthenic acids, and other organic substances. Collectors cover the surface of the hydrophilic mineral particles with a hydrophobic film making them float.

In some cases, it is necessary to make it difficult for individual minerals to rise to the surface. To this end, agents known as **suppressors** or **depressors** are added to the suspension. Suppressors are alkalis and alkali salts, such as cyanides, silicates, and sulphates. These agents render the surface of minerals more hydrophilic and thus make it difficult for them to rise to the surface.

Frothers, collectors, and depressors are called **flotation agents**.

The use of flotation agents makes it possible to enrich a great variety of rocks. The amount of a flotation agent used is insignificant (100 g per 1 t of rock). Flotation is now extensively employed as an industrial method for large scale beneficiation of raw materials.

Thermal beneficiation is based on the different fusibility of materials which are present in a mixture. For example, sulphur, having a low melting point of 119 °C as compared with the gangue in sulphur ore (m.p. is above 1000 °C), is smelted from ore in molten form.

Chemical methods of beneficiation are rather varied. They include selective dissolution, decomposition by chemical reactants, and roasting.

Liquids are enriched (concentrated) by evaporating the solvent, adding the valuable component to the solution (after saturation), and precipitating impurities from the solution or converting them to a gaseous state (evaporation of impurities by desorption).

Gas mixtures are enriched using the differences in the properties of gases in a mixture. It is common knowledge that any gas may, under certain conditions, be converted to a liquid. There exists a specific temperature for each gas at which it becomes liquefied (the condensation temperature or, similarly, the boiling point). A *method of consecutive (fractional) condensation* is based on the difference in gas condensation temperatures. For example, this method is employed to separate a coke-oven gas consisting of hydrogen, nitrogen, carbon monoxide (CO), methane (CH_4), and ethylene (C_2H_4). All these gases are transformed into a liquid at different temperatures, i.e. they have different condensation temperatures (°C):

Ethylene	−103	Nitrogen	−195.7
Methane	below −161	Hydrogen	−252.6
Carbon monoxide	−191.7		

The gas is first cooled to a temperature lower than the ethylene condensation temperature, but higher than the methane condensation temperature. In this case, only ethylene among all the gases is transformed into a liquid. The remaining components stay in a gaseous state. Liquid ethylene is separated, and the remaining gaseous mixture is now cooled to a temperature lower than the methane condensation temperature, but higher than the carbon monoxide condensation temperature. Here, methane is transformed into a liquid and recovered from the mixture. The remaining gaseous mixture is treated in a similar manner. Thus, while gradually cooling the mixture, it can be separated into individual gases.

Another method for enriching gases and liquids is **rectification.** It is based on the difference in the boiling points of various substances. This method is employed to separate air into nitrogen and oxygen. Air is composed predominantly of oxygen (20.95 per cent) and nitrogen (78.09 per cent). Liquid oxygen boils at a temperature of —182.95 °C, whereas liquid nitrogen boils at a lower temperature, —195.8 °C.

To separate air, i.e. to obtain pure oxygen and nitrogen, the air is preliminarily cooled and converted to the liquid state. This liquid mixture is then partially evaporated. Since nitrogen boils at a lower temperature than oxygen, the former evaporates more readily and its vapours are present over the liquid in larger quantities than in the liquid itself. The vapour over the liquid becomes nitrogen rich and the liquid becomes nitrogen poor and, hence, enriched in oxygen. If the vapours are separated from the liquid, the air will be partially separated, since the vapours contain more nitrogen, and the liquid contains more oxygen. Repeating this technique many times, air can be completely separated into nitrogen and oxygen.

The rectification method is based on this type of multiple partial evaporation of a liquid, in combination with steam condensation. (Rectification processes are dealt with in more detail in the chapters describing individual production processes.)

The absorption method for the separation of gas mixtures is based on the fact that liquid solvents are capable of selectively absorbing some gas from a gas mixture. The gas mixture is passed through a liquid solvent (absorbent). The solvent is selected so that it dissolves only the gas to be recovered. The solvent with the absorbed gas is then directed to the next procedure (desorption) where the absorbed gas is recovered, in the concentrated form, from the solvent.

Not only liquid, but also solid materials may be used to adsorb individual gases from a mixture. This process is called **adsorption**. Adsorbed gases are desorbed (removed) from the surface of an adsorbent (solid material).

Absorption-desorption and adsorption-desorption methods for the separation of liquid and gas mixtures are being employed on a very wide scale in the chemical industry.

2.3 Water for the Chemical Industry

Water has exceptionally wide and various applications in the chemical industry. It is used as a raw material and a reactant in a number of industries (in the production of sulphuric acid (H_2SO_4) and nitric acid (HNO_3), for the manufacture of soda (Na_2CO_3), sodium hydroxide (NaOH), potassium hydroxide (KOH), and hydrogen; it is also employed in the hydrolysis and hydration processes).

In many industries, water functions as a solvent of solid, liquid, and gaseous substances to prepare aqueous suspensions of solid substances, such as suspensions and pulps (for example, when gravity and flotation concentration are used). Water is essential for washing solid and gaseous materials to remove impurities.

Water also functions as a cooling agent and a heat-transfer agent when cooling and heating solids or reactants. Various coolers and heaters are used for cooling and heating reacting materials with water or vapour. The basic source for both industrial and domestic water is **natural water**. Natural water is subdivided into atmospheric water (precipitated water), surface water, i.e. water from rivers, lakes and seas; and underground water (well, spring, deep-well, and mineral water).

Natural water contains suspended coarsely dispersed and colloidal organic and inorganic particles (sand, clay, etc.). It contains dissolved gases and salts, such as bicarbonates, sulphates, chlorides, nitrates of calcium, magnesium, and potassium. Various bacteria, fungi, or other microorganisms may be present in water.

The presence of coarsely dispersed particles, gases, salts, organic substances, and microorganisms may have an adverse effect on some reactions, cause equipment to corrode, promote scale formation, cause pipelines and apparatus to clog and water in boilers and apparatus to foam, and impair flotation processes. Therefore, water must meet certain requirements with respect to the content of mechanical impurities, dissolved salts, and gases before use in industry and the home.

The Characteristics of Water. Water quality is determined by its physical and chemical characteristics. The basic qualitative indices of water are: hardness, total salt content, oxidizability, transparency, colour, odour, and reaction.

Hardness is a property of water determined by the presence of dissolved calcium and magnesium salts. Hardness may be temporary or permanent.

Temporary hardness is determined by the presence of water-soluble bicarbonates of calcium, $Ca(HCO_3)_2$, and magnesium, $Mg(HCO_3)_2$. When water boils, these salts decompose and calcium carbonate, $CaCO_3$, precipitates from solution:

$$Ca(HCO_3)_2 = CaCO_3 + H_2O + CO_2 \qquad (2.3)$$

Permanent hardness is determined by the presence of chlorides and sulphates of calcium and magnesium. Boiling of water does not remove these salts.

There are great difficulties in handling hard water. When hard water boils, an insoluble precipitate of calcium carbonates or basic magnesium salt is formed from calcium and magnesium sulphates. This precipitate is deposited as scale on the internal surface of the pipes in boilers. Scale reduces heat transfer through the pipe walls, which causes their overheating and premature wear. Therefore, salts that cause hardness should be removed from water.

The total salt content measures mineral and organic impurities in water.

Oxidizability is a property of water determined by the presence of organic substances in it. The drinkability of water, length of storage, and industrial applications are dependent on the content of organic substances.

Transparency is measured by the thickness of a layer of water through which the image of a cross or a certain type can be observed either visually or by means of a photoelectric cell.

Reaction of water is its acidity or alkalinity, generally characterized by a pH value. The pH value is the negative decimal logarithm of the concentration of hydrogen ions $[H^+]$ in solution. The pH may vary from 1 to 14. For a neutral solution, the pH value is 7. As the solution becomes more acidic, the pH decreases, while as alkalinity increases, the pH increases.

Depending on the purpose, water may conventionally be subdivided into water for industrial and that for domestic use.

Water for domestic use should primarily be free from bacteria. It should also meet special requirements with respect to taste, colour, and odour.

Industrial water should not contain large amounts of dissolved salts. The maximum possible concentration of dissolved salts is established by the GOST standards for the industry which uses the water. For example, water used in the manufacture of synthetic fibres should meet the following requirements: the content of suspended particles does not exceed 20 to 40 mg per 1 litre, and the total salt content does not exceed 1.0 to 1.5 mg/litre. Water used in boilers should also be free from carbon dioxide and oxygen, which cause corrosion of pipes.

Water Preparation. Depending on the requirements, the preparation process is carried out in several steps. The major step includes removing suspended impurities from the water, softening (removal of hardness), desalination, degassing (removal of dissolved gases), and purifying the water (removal of organic impurities and microorganisms).

Water is cleaned of *suspended impurities* by settling or filtration, generally through a layer of sand or gravel. Organic impurities are present in water as superfine particles that are difficult to remove and which form stable *colloidal systems*. To remove colloidal particles, special **coagulants** are added. They promote adhesion of the fine particles to form more or less larger ones. The resulting flakes settle down. Aluminium sulphate is used as a coagulant to precipitate organic impurities from water. The precipitate is then removed by filtration; in this case some of the bacteria contained in water are also removed.

Water softening is one of the major water preparation processes. There are physical, chemical, and physicochemical methods for softening water. *Physical methods* primarily involve boiling water to remove salts causing temporary hardness. A *chemical method* reduces hardness by converting soluble calcium and magnesium salts to insoluble salts which form a precipitate that is filtered out later. To precipitate the calcium and magnesium salts, various chemical agents are added to water. When water is treated with lime milk, $Ca(OH)_2$, or with a caustic soda, NaOH, solution, the salts causing temporary hardness are removed. For example:

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3\downarrow + 2H_2O \qquad (2.4)$$

When soda, Na_2CO_3, is added to the water the salts causing permanent hardness are removed:

$$CaCl_2 + Na_2CO_3 = CaCO_3\downarrow + 2NaCl \qquad (2.5)$$

The combined **lime-soda method** is generally employed to soften water. Here, water is first treated with lime and then with soda, thus eliminating temporary and permanent hardness by causing all the calcium and magnesium salts to form insoluble precipitates as calcium carbonate, $CaCO_3$, and magnesium hydroxide, $Mg(OH)_2$.

To soften water, sodium phosphate, Na_3PO_4, is also used to precipitate the calcium and magnesium salts as calcium and magnesium phosphates (thus eliminating temporary and permanent hardness):

$$3Ca(HCO_3)_2 + 2Na_3PO_4 = Ca_3(PO_4)_2\downarrow + 6NaHCO_3 \qquad (2.6)$$

$$3MgCl_2 + 2Na_3PO_4 = Mg_3(PO_4)_2\downarrow + 6NaCl \qquad (2.7)$$

Ion-exchange methods are physicochemical methods for softening and desalting of water. They are based on the property that some poorly soluble substances, ion exchangers, exchange their ions for the ions of the salts dissolved in the water. For example, alumosilicate, $Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot nH_2O$, contains active sodium ions which pass into solution. In exchange for these ions, calcium or magnesium ions can be absorbed from the solution, clearing the water of these ions:

$$\begin{aligned} &Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot nH_2O + CaCl_2 \\ &\rightleftarrows CaO \cdot Al_2O_3 \cdot 2SiO_2 \cdot nH_2O + 2NaCl \end{aligned} \qquad (2.8)$$

Degassing of water removes noxious gases, such as hydrogen sulphide, sulphur dioxide, and carbon dioxide, which are capable of corroding equipment. The process is accomplished by purging water with air. The dissolved gases pass from the water to the air and are then removed together with the air. This process is also called **aeration.**

A big task for the national economy is the *purification of industrial waste water.* Waste water of many chemical enterprises contain impurities, such as acids, alkalis, salts, and diverse organic substances which are often toxic to plant and animal organisms. It is impermissible to discharge these waters into water reservoirs located close to chemical plants.

The processes that render waste water harmless are:

physicochemical processes including aeration, adsorption and evaporation with a view to precipitating impurities;

chemical processes including precipitation of impurities by various reactants followed by sedimentation and filtration of the precipitates;

biological processes are mainly used to purify waste water in residential areas by using microorganisms, for example, flaky colonies of bacteria and lower organisms contained in activated sludge. Microorganisms turn the organic impurities into carbon dioxide, nitrates, water, and oxides.

Water is consumed in millions of cubic metres at large integrated chemical plants. Therefore waste water, for example, water flowing out of coolers, is reused in the production processes in many industries. This water is called **recycled water**. It is cooled in special water reservoirs (ponds) (sometimes first sprayed), or pumped to the top of a wooden tower with a packing of grills and laths. As it flows down over the packing, the water is cooled by oncoming cold air. Such towers are called cooling towers.

2.4 Energy for the Chemical Industry

Chemical industries consume considerable quantities of energy. Energy is used not only for carrying out chemical reactions, but also for transporting materials, crushing and grinding solid substances, filtration, and compression of gases.

Currently, the chemical industry is the most power-consuming industry. For example, the manufacture of 1 t of calcium carbide requires at least 3500 kW of electric power. Energy consumption for calcium carbide makes up about half its production cost, and 35 to 50 per cent of the cost goes for polyvinyl chloride and polyethylene. About 14 000 kW are needed in the manufacture of each ton of nitrogen fertilizers whose production is increasing. This is far from being a comprehensive list on energy consumption in the chemical industry. It is clear from these examples that the energy usage in the chemical industry is of tremendous importance.

Sources of Energy. The sources of energy used to manufacture chemical products include coal, petroleum, oil shales, natural gases, and hydroelectric- and atomic stations. The sources differ in energy values. The **energy value** is the quantity of energy (in kilowatt-hours) that can be produced by the combustion of 1 kg or 1 cubic metre of fuel. The energy values (kW·h/kg) of some fuels are:

Coal	8.0
Coke	7.2
Peat	4.0
Coke gas	4.8
Natural gas, kW·h/m^3	10.6

The desirability of using some energy sources is determined not only by their energy value, but also by their natural reserves, geographic location, accessibility, and other factors.

Types of Energy. Electric, thermal, chemical, luminous, nuclear energy, and secondary energy resources are used in the chemical industry.

The use of *electric energy* at chemical plants permits large-scale realization of electrochemical processes used to decompose substances by applying electric current to produce, for example, chlorine, hydrogen, oxygen, alkalis, and metals. Conversion of electric to thermal energy when using electrothermal processes produced temperatures of 1350 to 3500 °C. This could not be accomplished by any other processes. This resulted in the development of a method for using carbon to reduce metal oxides to form free metals, such as iron and zinc, and also in discovering carbides, i.e. carbon-metal compounds, like calcium carbide, which is used as a raw material for the production of acetylene. The latter contributed to the manufacture of materials, such as plastic materials, synthetic rubbers, and fibres, which are synthesized from acetylene.

It is common practice to convert electric energy to mechanical energy, which is essential for the transportation of materials, for crushing purposes, compression of gases, etc.

Thermal energy accounts for more than two thirds of the energy consumed in the chemical industry.

Chemical energy is used in galvanic cells and storage batteries where it is converted to electric energy.

Luminous energy is provided by the Sun. The Sun emits 2.86×10^{33} kW per second into outer space, from which the Earth receives only 2×10^{-7}, thus maintaining a great variety of forms of life on our planet. Conversion of solar to electric energy at helium installations presents some interest. However, the cost of electric energy obtained in this way exceeds the cost of energy from conventional hydroelectric stations by many times.

Photosynthesis as a producer of energy is quite promising and has been put to practice. In photosynthesis, chemical reactions occur when exposed to light. Hydrogen chloride and some other organic compounds have been synthesized in industry.

Nuclear energy is widely used to produce electric energy. By the end of the current century, atomic electric stations will generate about half of all electric energy; this will allow power-consuming chemical industries to expand, particularly, the electrochemical processes for metal production. Chemical radiation processes are being more extensively used when reactions occur under the effect of radioactive radiations.

Secondary energy resources—waste energy, or industrial products having a high temperature, are used to meet the energy requirements of enterprises, thus reducing environmental losses.

The Rational Utilization of Energy. The chemical industry consumes large quantities of energy and this, in many respects, determines the cost of products. One of the major problems is the rational utilization of energy. *The energy utilization factor is the ratio of the amount of energy which is theoretically consumed in producing a unit of product to the amount of energy actually consumed.* This factor is an evaluation or criterion for the rational utilization of energy.

Among all the types of energy, thermal energy is consumed in the greatest quantities by chemical plants. The degree of utilization of thermal energy is characterized by *the thermal efficiency expressing the ratio of the amount of heat usable in carrying out the basic chemical reactions to the total amount of heat consumed.*

This factor is low in many industries. For example, when roasting limestone at 900 °C

$$CaCO_3 = CaO + CO_2 \qquad (2.9)$$

the energy utilization factor is about 65 per cent. Here, 25 per cent of the heat is lost together with products escaping the apparatus (CaO and CO_2), and 10 per cent is lost to the environment. Because of this, chemical plants face the problem of how to use heat from gases, liquids, and solids (recovery of heat) escaping the reaction apparatus, and how to use energy from compressed gases and liquids (recovery of energy).

The heat sources may be chemical reactions that occur with heat evolution. Let us assume that the exothermal reaction $A + B \rightleftarrows R + Q$ occurs. To maintain a high reaction rate, a high temperature, e.g. 500 °C is required. This high temperature can be reached without an external heat supply to the reactor, if the preheated reactants are admitted into it. What can be used as a heat-transfer agent? Hot reaction products can be used for heating the reaction gases, the former give off their heat to the gases in heat exchangers which are admitted into the reactor. Thus, the chemical reactions occur at high temperatures without using external heat. Such processes are called **autothermal processes.**

The reaction heat may be used not only for heating the products being admitted, but also for the production of steam, the energy of which is used, for example, for the compression of reaction gases.

The heat from heated waste gases is most frequently used for preheating materials admitted into a reaction apparatus or for producing steam which is essential to industry. Heat recuperators and regenerators, and waste-heat boilers are types of heat exchangers used for this purpose.

The **recuperator** (Fig. 6) is usually a cylindrical apparatus *2*. The inside accommodates plates *1* with tubes expanded in them. The hot gases flowing out of the reaction apparatus pass along recuperator tubes *3*, while the cold gases, to be fed into the reaction apparatus, flow in the intertube space. The cooling of hot gases and the heating of cold gases are effected by heat exchange through the tube walls.

The **regenerator** is a periodically operating chamber filled with a packing (Fig. 7). The hot gases flowing out of the reaction apparatus are first allowed to pass through chamber *1*. The gases contacting packing *2* give off their heat to it and become cool, the packing becoming hot. The supply of hot reaction gases is then discontinued, and the cold gases are allowed to pass through the hot packing, to be fed into the reactor. The cold gases take up the heat from the packing and become hot, the packing becoming cool. The hot gases are then purged through the cooled packing.

In order to make the process continuous, at least two regenerators are installed. In this case, when one chamber is used for heating the packing, i.e. the hot gases are allowed to pass through it, the cold gas is allowed to pass in the other chamber, i.e. the packing gives off its heat to the cold gas. After a certain period of time, there is an automatic changeover of gas streams.

Regenerators are generally employed for using the heat of gases having a very high temperature of about 700 to 800 °C or higher. Recuperators are generally installed for using the heat of gases and liquids having lower temperatures.

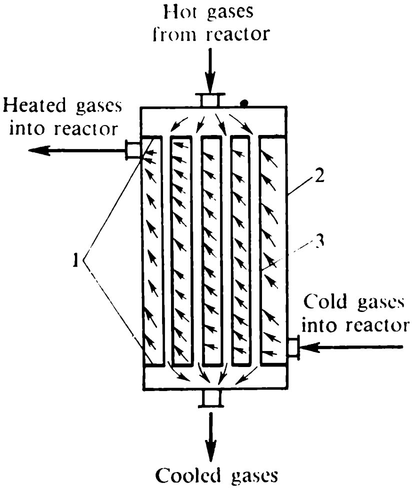


Fig. 6. Recuperator

1—plates; *2*—apparatus body; *3*—tubes

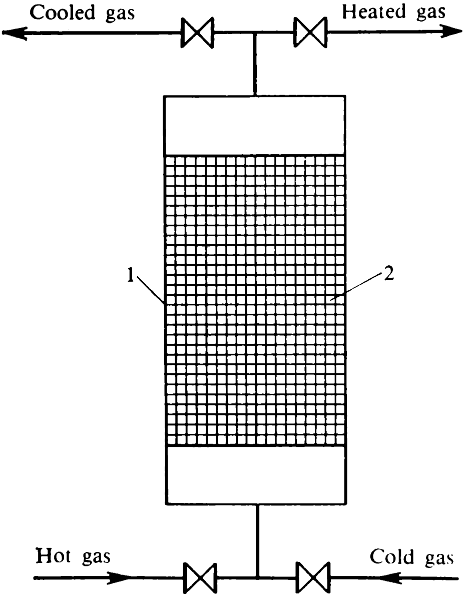


Fig. 7. Regenerator

1—chamber; *2*—packing

As has been mentioned, *waste-heat boilers* are employed when the heat of waste gases is used for the production of steam. Figure 8 shows the construction of a waste-heat boiler. The hot gases flow along tubes *4* located in the body of boiler *3*. Water is admitted into the intertube space of the boiler through pipe connection *5*. The resulting steam is discharged through moisture separator *2* and valve *1*.

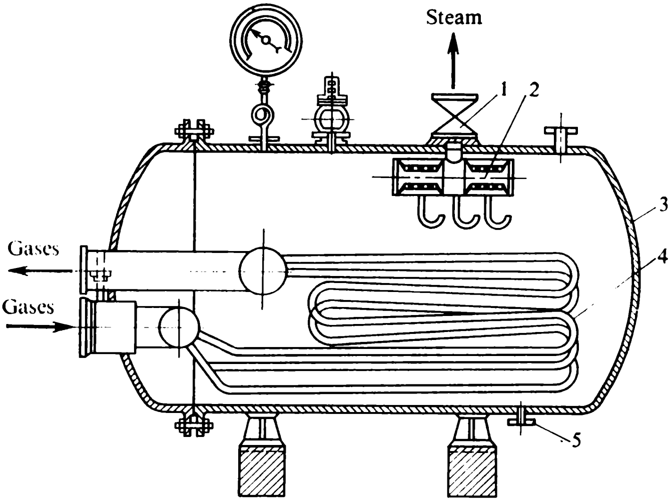


Fig. 8. Waste-heat boiler

1—valve; *2*—moisture separator; *3*—boiler shell; *4*—tubes; *5*—pipe connection

The heat of waste gases is sometimes used for heating air or water used in the heating of factory buildings and also for other purposes (hot water for shower baths, hotbed farms, etc.).

The energy of compressed gases or liquids flowing out of the reaction apparatus is used to set the wheels of gas or water turbines mounted on the same shaft in rotation, together with a pump and an electric motor, which then reduce the consumption of electric energy which feeds the electric motor.

Nowadays, the heat of waste gases and the energy of compressed gases or liquids are being widely used, thus allowing energy efficiencies to be considerably improved. Such processes have found application in power technological processes. The development of the latter processes is typical of the modern chemical industry.

REVIEW QUESTIONS

1. Into what groups are raw materials for the chemical industry subdivided?
2. Why is it necessary to enrich raw materials?
3. Name the methods of beneficiation of solid rocks.
4. What principle is gravity concentration based on?
5. What principle is electromagnetic concentration based on?
6. What minerals are called hydrophobic or hydrophilic?
7. What phenomenon is a method of beneficiation by flotation based on?
8. Give an example of the integral utilization of raw materials.
9. What water is called hard and how is the hardness of water reduced?
10. What types of energy are used in the chemical industry?
11. What task is accomplished by recuperators, heat regenerators, and waste-heat boilers?
12. What is the essence of power technological processes?

Chapter 3

BASIC REGULARITIES OF CHEMICAL TECHNOLOGICAL PROCESSES

3.1 The Concept of a Chemical Technological Process

Any chemical technological process should meet certain requirements. First of all, chemical technological processes should be carried out preferably under conditions that permit obtaining the maximum yield of a product, i.e. the largest amount of the product from an initial amount of raw materials. It is very important that the conditions allow the process to go at a high rate. The higher the rate, the more starting substances will be processed into products by an apparatus per hour, i.e. as the process rate increases, the equipment becomes more productive. And, finally, it is no less important that the resulting product be cheap and possess a high quality.

To meet the requirements listed above, the process should be carried out under optimal conditions.

The optimal process conditions are those most advantageous combinations of process parameters (such as temperature, pressure, concentration of the starting reactants, etc.) that give the maximum yield of the product at a high rate and reduce the consumption of raw materials, energy, fuel, cut down the expenses for construction and operation of equipment, and for the labour expenditure in the manufacture of the product. All stages of technological processes should be carried out under optimal conditions. It is impossible to choose the optimal conditions without a knowledge of the basic regularities that govern chemical technological processes.

For chemical reaction to occur, it is essential that the starting substances have contact with each other. Therefore, a chemical transformation includes a number of interrelated elementary processes, namely: the supply of the reactants to the reaction zone, the chemical reactions themselves, and removal of the products from the reaction zone. For example, to burn coal in atmospheric oxygen, it is essential that the oxygen molecules leave the air-filled space to the surface of solid particles. Reaction with carbon (the basic constituent of coal) is an oxidation reaction:

$$C + O_2 = CO_2 \tag{3.1}$$

The resultant carbon dioxide, CO_2, is removed from the surface of the solid coal particle (Fig. 9).

If the air stands motionless around the solid coal particle, the supply of oxygen and removal of carbon dioxide will be accomplished only by random motion of the gas molecules, i.e. by **molecular diffusion.** In a moving medium, when a current makes the air move around the coal particles, the O_2 and CO_2 are transferred not only by molecular diffusion, but also by the medium itself along the direction of its motion, i.e. by **convection**. When the reactants are intensely stirred, convective transfer is also called **turbulent diffusion.**

Many chemical processes are multiphase ones, i.e. they consist of a plurality of phases existing simultaneously. A phase includes homogeneous parts of the system, identical in composition, physical and chemical properties, and separated from the other parts of the system by the interface. The reactants of any reaction may exist in the solid phase (S), the gaseous phase (G), or the liquid phase (L).

The previously mentioned process of coal oxidation with atmospheric oxygen is an illustration of a multiphase process. This process has two phases: a gaseous phase (G) and a solid phase (S). The gaseous phase incorporates one of the starting reactants, oxygen, and a reaction product, carbon dioxide, whereas the solid phase incorporates a second reactant, carbon. The absorption of sulphur trioxide, SO_3, by water is an illustration of a two-phase process involving a gas and a liquid (G-L):

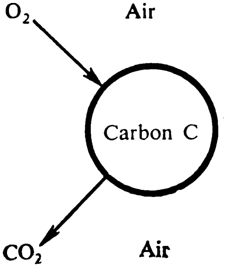


Fig. 9. Diagram of coal combustion in the air

$$SO_3 + H_2O = H_2SO_4 \tag{3.2}$$

There are processes that include all the three phases; solid, liquid, and gaseous. Supplying reactants to the reaction zone and removing the products from the reaction zone in multiphase processes include transfer of substances from one phase to another. For instance, in the latter example, the chemical reaction of absorption of sulphur trioxide with water may be carried out only when SO_3 is transferred from the gaseous phase to the liquid phase, and then made to react. Processes for transferring substances from one phase to another are called **mass transfer.**

3.2 Classification of Chemical Reactions

The study of the most essential stage of the chemical technological process, chemical transformations, is extremely important in chemical technology. Chemical reactions that occur in industrial processes are quite varied. They are classified according to various criteria.

Reactions are subdivided according to **reaction conditions** into: (1) *isothermal reactions* that occur at constant temperatures and *non-isothermal reactions* in which temperatures are not constant; (2) *reactions that occur at constant or variable volumes* (*pressures*); (3) *adiabatic reactions* (without outside supply of heat or removal of heat to the environment) and *non-adiabatic reactions* (when heat exchange occurs with the environment).

Reactions are subdivided according to the **phase state** of reactants into *homogeneous* and *heterogeneous reactions.* In homogeneous reactions all the reactants are in the same phase, gaseous (G), liquid (L) or solid (S). The oxidation of nitric oxide, NO, with oxygen is an example of a homogeneous reaction that occurs in the gaseous state:

$$\underset{G}{2NO} + \underset{G}{O_2} = \underset{G}{2NO_2} \qquad (3.3)$$

The initial substances and reaction products are gases. A homogeneous process in which liquid substances, e.g. NaOH and HCl solutions, are involved, is called a liquid phase process:

$$\underset{L}{NaOH} + \underset{L}{HCl} = \underbrace{NaCl + H_2O}_{L} \qquad (3.4)$$

The reactants in heterogeneous processes are of different phases. Two or more phases are present simultaneously in the reaction volume. For example, substances that react chemically in two-phase systems may be found to be in the following physical states: gas-liquid (G-L), gas-solid (G-S), liquid-solid (L-S), liquid-liquid (L-L), provided that liquids are not mixed, and solid-solid (S-S). There is an interphase in all heterogeneous processes. The combustion of coal described before is an illustration of a heterogeneous process in which gaseous and solid (G-S) phases are involved:

$$\underset{S}{C} + \underset{G}{O_2} \overset{\bullet}{=} \underset{G}{CO_2} \tag{3.1}$$

The absorption of sulphur trioxide with water is an example of the G-L system:

$$\underset{G}{SO_3} + \underset{L}{H_2O} = \underset{L}{H_2SO_4} \tag{3.5}$$

The reaction between sulphuric acid, H_2SO_4, and copper oxide, CuO, is an example of the heterogeneous L-S system:

$$\underset{L}{H_2SO_4} + \underset{S}{CuO} = \underbrace{CuSO_4 + H_2O}_{L} \tag{3.6}$$

According to the **mechanism of reactions**, they are subdivided into *simple*, *concurrent*, and *consecutive reactions*. All these reactions may be classed as **reversible or irreversible**. The simple irreversible reaction is characterized in that, as it proceeds, the starting material is completely transformed into a reaction product and the concentration of the starting reactant is reduced from its initial value to zero. Combustion of sulphur is an example of an irreversible reaction:

$$S + O_2 \rightarrow SO_2 \tag{3.7}$$

This reaction proceeds until the whole of sulphur is consumed and converted to sulphur dioxide, SO_2. Irreversibility is designated by an arrow directed to one side.

Reversible reactions differ from irreversible reactions in that the resulting reaction products are capable of being converted back into the initial substances. For example, the reaction between hydrogen, H_2, and iodine vapours, I_2, gives a gaseous product, hydrogen iodide, HI:

$$H_2 + I_2 \rightleftarrows 2HI \tag{3.8}$$

It is not possible to convert completely iodine and hydrogen into hydrogen iodide, since part of the resulting hydrogen iodide again decomposes to form the starting reactants, iodine and hydrogen. In such cases, the reaction is said to proceed both in the forward and the reverse direction, i.e. it is reversible. Reversibility is designated by reverse arrows in the equation. As the initial substances cannot be converted completely into products during reversible reactions, both the reaction products and the initial substances are simultaneously present in the reactor.

During **concurrent reactions** involving the same initial substances, several different transformations occur to form different products. For example, the reaction between gaseous ammonia and oxygen causes several reactions to form simultaneously various products: nitric oxide, NO, nitrous oxide, N_2O, and nitrogen, N_2:

$$4NH_3 + 5O_2 = 4NO + 6H_2O \tag{3.9a}$$

$$4NH_3 + 4O_2 = 2N_2O + 6H_2O \tag{3.9b}$$

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O \tag{3.9c}$$

During **consecutive reactions**, the initial substance is not immediately converted into the final product since an intermediate product is first formed, from which the final product is obtained. For example, the oxidation of sulphur pyrite with oxygen finally produces sulphur dioxide, SO_2, and ferric oxide, Fe_2O_3:

$$4FeS_2 + 11O_2 = 8SO_2 + 2Fe_2O_3 \tag{3.10}$$

These products are not produced immediately, but through an intermediate stage. The sulphur pyrite first decomposes at high temperature into ferrous sulphide, FeS, and sulphur, S:

$$FeS_2 = FeS + S \tag{3.10a}$$

Only after that are the ferrous sulphide and sulphur oxidized with oxygen to form the final products, SO_2 and Fe_2O_3.

In developing chemical technological processes, the following two problems should be resolved.

1. What maximum amount of a product can be derived from a given raw material?

2. How long will it take to effect a chemical transformation, or, in other words, what is the rate of the process?

The first problem can be answered by chemical equilibrium theory, i.e. the statics of the process. The theory on chemical process rates called chemical kinetics gives the answer to the second problem. The study of the equilibrium and kinetics of the process is exceptionally important for chemical technology. Along with the general regularities, such as the law of mass conservation and the law of energy conservation, it permits selecting the best technological conditions, i.e. the most suitable combination of the basic values (parameters of the conditions) that have an effect on the yield and quality of the product and the rate for its production. The basic parameters for most processes include temperature, pressure, the use of catalyst, and the concentration of reactants.

3.3 Chemical Equilibrium in Technological Processes

Most industrial chemical reactions are reversible. In such cases, chemical transformations occur in two directions. The reaction between carbon monoxide, CO, and water vapours (carbon monoxide conversion), which is widely used in the chemical industry to produce hydrogen, is an illustration of the reversible process:

$$\underset{\text{vapour}}{CO + H_2O} \rightleftarrows H_2 + CO_2 \qquad (3.11)$$

By following the forward reaction (from the left to the right) the initial substances (carbon monoxide and water) are transformed into the reaction products (hydrogen and carbon dioxide). These resulting products then begin reacting with each other to form once again the initial substances, i.e. the reverse reaction occurs (from the right to the left). Both reactions proceed simultaneously.

At the beginning of the process, the concentrations of the initial substances, CO and H_2O, are great and the forward reaction rate is therefore considerable. But as the process continues, the amounts of carbon monoxide and water vapour grow smaller, their concentrations become lower, and the forward reaction is gradually slowed down. The amounts of the products, hydrogen and carbon dioxide, simultaneously grow, their concentrations increase, and the reverse reaction rate is therefore enhanced. Finally, a moment comes when the rates of the forward and reverse reactions are equal. This state in the reaction system is called **chemical equilibrium.**

Since, in actual fact, the starting reactants in reversible processes are not completely transformed into the reaction products the starting reactants and the reaction products, CO, H_2O, CO_2, H_2, are both present after the equilibrium has been established in the system; specific CO, H_2O, CO_2, and H_2 concentration levels are attained at equilibrium and remain unchanged. They remain constant not because chemical transformations have ceased, but because the forward reaction is balanced by the reverse reaction. The number of CO and H_2O molecules involved in the reaction for a certain period of time (the forward reaction) is equal to that resulting from CO_2 and H_2 interreacting for the same period of time (the reverse reaction).

The Equilibrium Constant. The specific ratio between the concentrations of substances CO, H_2O, H_2 and CO_2 in the equilibrium system will remain constant until external conditions (e.g. temperature) have changed.

The ratio of the product of concentrations of the reaction products to the product of the concentrations of the initial substances at the moment of equilibrium is called the equilibrium constant. Here, the concentrations of the initial substances and reaction products should be used at levels that are equal to the coefficients for the given substances in the reaction equation.

For example, for reaction (3.11) the equilibrium constant K_{eq} is expressed as

$$K_{eq}=\frac{C_{H_2}\cdot C_{CO_2}}{C_{CO}\cdot C_{H_2O}}$$

where C_{H_2}, C_{CO_2}, C_{CO}, and C_{H_2O} are H_2, CO_2, CO, and H_2O concentrations, respectively, at the moment of equilibrium.

The equilibrium constant is used for calculating the equilibrium in reversible processes.

The degree of conversion and the chemical yield attained at equilibrium are called the *equilibrium degree of conversion* and *equilibrium yield*. Both the equilibrium degree of conversion and the equilibrium yield are said to be maximum for the given conditions. The equilibrium state may be estimated by their values, i.e. one can determine to what extent the equilibrium has been shifted to the right or left side. However durable the process may be after equilibrium is reached, it is impossible to attain a degree of conversion and chemical yield greater than at equilibrium. They can be improved if the reaction equilibrium is shifted to the right by varying external conditions. Therefore, it is important to have an idea how various technological parameters (such as temperature, pressure, and the concentration of reactants) affect chemical equilibrium.

The Effect of Various Factors on the Equilibrium of Reversible Reactions. The Le Chatelier Principle. The effect of temperature, pressure, and the reactant concentrations on the equilibrium in homogeneous and heterogeneous processes is defined by the Le Chatelier principle, which was discovered in 1884. This principle states that *if a system at equilibrium is acted upon externally, thus varying some of the values that determine the equilibrium state, the equilibrium is shifted in such a way as to make the effect of action less pronounced.*

Temperature, pressure and the reactant concentrations are the major factors that affect an equilibrium shift in a reversible reaction.

Temperature Effect. To determine temperature effect on the equilibrium shift in a reversible reaction, it is essential to know whether the given reaction is exothermic (i.e. the one that goes left to right and evolves heat, $+Q$) or endothermic (the one that goes left to right and absorbs heat, $-Q$).

The conversion of carbon monoxide with water vapour dealt with above relates to **reversible exothermic reactions:**

$$CO + \underset{\text{vapour}}{H_2O} \rightleftarrows H_2 + CO_2 + Q \qquad (3.11)$$

If, after the equilibrium is reached in this system, the temperature is changed, e.g. lowered, according to the Le Chatelier principle, changes should take place in the system that will compensate for the lowered temperature by raising it. Consequently, the reaction that evolves heat will take place, i.e. new CO and H_2O portions will be converted into CO_2 and H_2. The reaction equilibrium is thus shifted to the right and the equilibrium yield increases.

If the temperature is raised for exothermic reactions, the equilibrium will be shifted to the left and the equilibrium chemical yield will decrease, Figure 10 shows variations in the degree of conversion for reversible exothermic reactions during temperature fluctuations. The equilibrium state is judged by the equilibrium degree of conversion, i.e. the higher the equilibrium degree of conversion, the more the reaction equilibrium is shifted to the right. It is apparent from Fig. 10 that as the temperature rises, the equilibrium degree of conversion becomes lower and, hence, the reaction equilibrium is shifted to the left. To shift it to the right and attain a high degree of conversion and the high chemical yield, the temperature should be lowered.

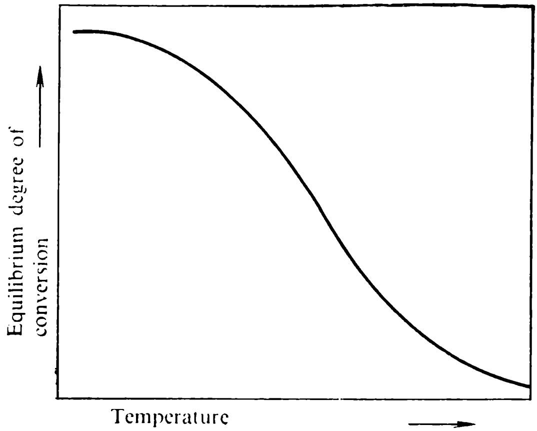


Fig. 10. The effect of temperature on the equilibrium degree of conversion for reversible exothermic reactions

It is the opposite for **reversible endothermic reactions.** Lower temperatures lead to a shift of the equilibrium to the left and a decreased chemical yield, whereas higher temperatures lead to a shift of the equilibrium to the right (Fig. 11).

The Effect of Pressure. If reversible reactions proceed with variations in volume, apart from temperature, the equilibrium state of such reactions is affected by pressure. For example, the reversible reaction for synthesizing ammonia proceeds in the gaseous phase from the left to the right when the volume is reduced:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad (3.12)$$

Here, four molecules of the initial substances produce two molecules of the final product. As the pressure increases in the system at equilibrium, changes should take place which, according to the Le Chatelier principle, will lead to a lower pressure or, what appears the same thing, fewer molecules present in the gas mixture. The forward reaction is such a process. Therefore, certain amounts of nitrogen and hydrogen are additionally transformed into ammonia, the equilibrium is shifted to the right and the ammonia yield increases. As the pressure becomes lower in the reaction occurring with smaller volume, the equilibrium is shifted to the left. The effect of pressure on the equilibrium degree of conversion for such a reaction is shown in Fig. 12.

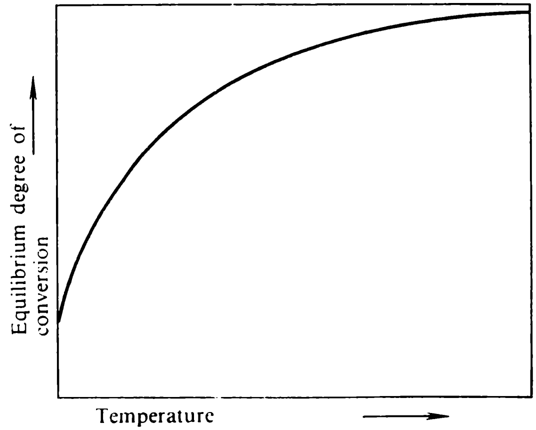


Fig. 11. The effect of temperature on the equilibrium degree of conversion for reversible endothermic reactions

It is the opposite for reactions proceeding with larger volume. As the pressure becomes lower the chemical yield increases, and as the pressure becomes higher the chemical yield decreases. Reaction between methane, CH_4, and water vapour (methane conversion) is an illustration of such a reaction:

$$\underset{\text{vapour}}{CH_4 + H_2O} \rightleftarrows 3H_2 + CO \qquad (3.13)$$

The Effect of the Concentration of the Reactants. The final product yield may be increased by varying the concentrations of the substances involved in the reactions. If, for example, after the equilibrium has been reached in the conversion of carbon monoxide:

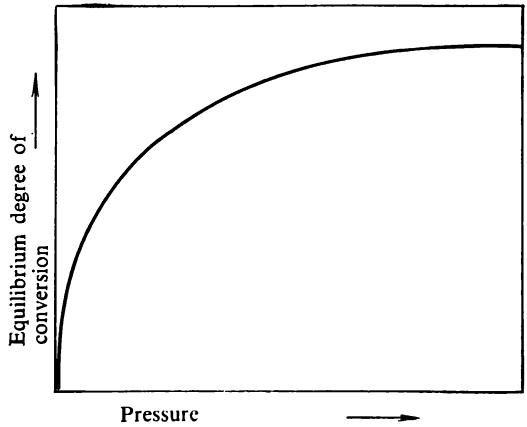


Fig. 12. The effect of pressure on the equilibrium degree of conversion for reversible reactions occurring with reduced volume

$$\underset{\text{vapour}}{CO + H_2O} \rightleftarrows H_2 + CO_2 \qquad (3.11)$$

the concentration of the starting reactants (CO or water vapour) is increased, according to the Le Chatelier principle, processes should occur that will bring down the concentration of these reactants, i.e. CO and H_2O should react. The equilibrium is thus shifted to the right and the chemical yield increases. The usual practice is not to increase the concentrations of all the starting reactants but to use a cheaper reactant in an excess amount. In the previous example, this reactant is water, and therefore, water vapour is used in an excess amount. The equilibrium can be shifted not only by increasing the concentrations of the initial substances, but also by lowering the concentrations of the reaction products. This can be accomplished by removing the products from the reaction system.

Reversible processes are widely employed in chemical technology. When choosing conditions for such processes, the requirements should be set to shift the equilibrium so as to form the reaction product. When doing this, the following should be borne in mind: to increase the equilibrium yield, it is essential

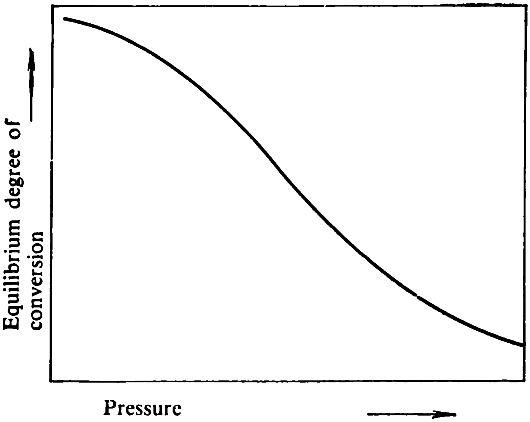


Fig. 13. The effect of pressure on the equilibrium degree of conversion for reversible reactions occurring with increased volume

(1) to lower the temperature for exothermic reactions;

(2) to raise the temperature for endothermic reactions;

(3) to raise the pressure in reactions using a smaller volume;

(4) to reduce the pressure in reactions using a larger volume;

(5) to raise the concentration of the starting reactants;

(6) to reduce the concentration of the reaction products.

It should also be taken into account that in order to shift the equilibrium, several parameters leading to increased chemical yield should (when possible) be simultaneously varied. These include temperature, pressure, and the concentrations of the reactants.

The cases listed above make it possible to establish the range of conditions when a high equilibrium chemical yield can be attained. But it is not sufficient to know these conditions only to implement a process, for in addition to a high chemical yield, a high process rate is needed since apparatus productivity is largely dependent on the latter.

3.4 The Rate of a Chemical Technological Process

Enhancing reaction rates is especially important in large huge-scale modern industries that employ expensive apparatus and machines.

It is often the case that under the conditions when a high chemical yield can be attained, the reaction rate is low, or vice versa. Therefore, the final choice for the conditions can be made only after the kinetics of the process has been studied. Kinetics permits establishing what is the reaction rate of the initial substances and what it is dependent on. Taking into account the kinetics of the process, conditions may be chosen under which the reaction will not only result in a high yield, but will also proceed at a high rate.

The amount of the initial substances involved in reactions per unit time serves as the parameter for the rate of chemical reactions. For example, the rate of the oxidation of sulphur dioxide to sulphur trioxide with oxygen:

$$2SO_2 + O_2 \rightleftarrows 2SO_3 \tag{3.14}$$

can be estimated from the fact how rapidly the SO_2 concentration decreases. If it decreases rapidly, the reaction rate is said to be high; if the SO_2 concentration varies slowly, the reaction rate is said to be low. The reaction rate can also be determined by how rapidly the concentration of the products (in this case, SO_3) increases.

The rate of a chemical process is the variation in the concentration of one of the reactants or reaction products per unit time in the unit volume of the reaction mass.

In most cases chemical technological processes are complex reactions. The rate of these processes is dependent not only on the rate of the main reaction, but also on the rates of side reactions. For heterogeneous processes it is also dependent on the rate of supply of the starting reactants to the reaction zone and on the rate of removal of the products from the reaction zone.

The rates of individual reactions are exceedingly different. Reactions are known that occur very rapidly. For example, the oxidation of ammonia on a platinum catalyst is completed practically within a ten thousandth of a second, the neutralization reaction is completed within several seconds. Other reactions like iron oxidation proceed slowly.

The Effect of Various Factors on the Chemical Reaction Rate. The chemical reaction rate is primarily dependent on the nature of the reactants, i.e. on their physical and chemical properties. Besides, factors such as the concentrations of the reactants, temperature, pressure, catalysts, and the extent substances are stirred to have a substantial effect on the reaction rate.

The Effect of the Reactant Concentration. It is known that reactant molecules move at different rates in a reaction zone. To make a chemical reaction occur the molecules of various substances must collide with each other. For example, to produce hydrogen iodide (HI) from hydrogen and water vapour:

$$H_2 + I_2 = 2HI \tag{3.8}$$

it is essential that the iodine molecule should collide with the hydrogen molecule. The number of collisions of iodine molecules with hydrogen molecules depends on the number of these molecules present in the volume. The more reacting particles are present per unit volume, the greater the probability of their collision and, hence, the higher the reaction rate. Therefore, the chemical reaction rate is proportional to the concentration of substances involved in a reaction.

The rate of the production of hydrogen iodide (r_{HI}) according to the reaction just given is proportional to the hydrogen concentration C_{H_2} and the iodine concentration C_{I_2}:

$$r_{HI} = k_C C_{H_2} \cdot C_{I_2} \tag{3.15}$$

The quantity k_C in this rate equation is the **reaction rate constant** and depends on the nature of the reactants and reaction conditions.

In the general case, for the irreversible reaction:

$$nA + mB \rightarrow pR \tag{3.16}$$

the rate equation (kinetic equation) is expressed as follows:

$$r_R = k_C C_A^n C_B^m \tag{3.17}$$

where r_R is the reaction rate, C_A and C_B are concentrations of the initial substances A and B, and n and m are stoichiometric coefficients (coefficients in the reaction equation).

The Effect of Pressure. The concentration of a substance in the gaseous state increases as the pressure increases.

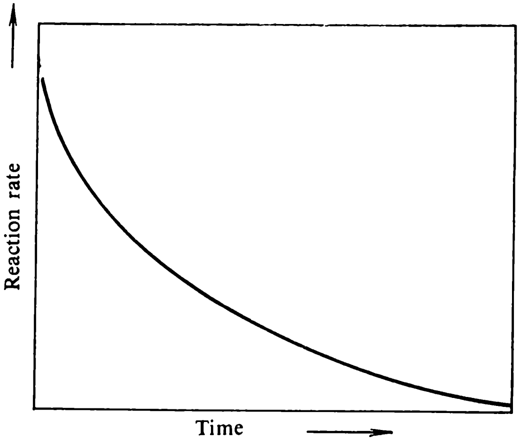


Fig. 14. A decrease in the reaction rate in the course of the reaction

Therefore, for reactions involving gaseous substances, a higher pressure (which means a higher concentration) brings about a higher reaction rate.

In carrying out chemical reactions, it should be remembered that at the beginning of the process, when the concentrations of the reactants are high, the reaction rate is high too. As the reaction proceeds, the concentrations of the reaction products increase, whereas the concentrations of the initial substances decrease, and the reaction rate is therefore very low (see Fig. 14). Hence, complete conversion of the starting reactants into the product requires a considerable period of time, which results in lower apparatus productivity. Therefore, it is not always desirable to attain complete conversion of the starting reactants into the product so that the apparatus productivity is not low.

In view of this, when reversible reactions are employed, the chemical yield is not brought to equilibrium.

The Effect of Temperature. It is known, that not all molecular collisions result in chemical conversions. Only active molecules enter into reactions. They possess a higher rate of motion and therefore exhibit higher energy as compared with the other molecules in the system. Heating the reaction mixture increases the number of active molecules that possess the energy necessary for them to enter into reactions. Therefore, a higher temperature is accompanied by a sharp increase in the chemical reaction rate (see Fig. 15). *A temperature rise of 10 °C increases the reaction rate by 2 to 4 times.*

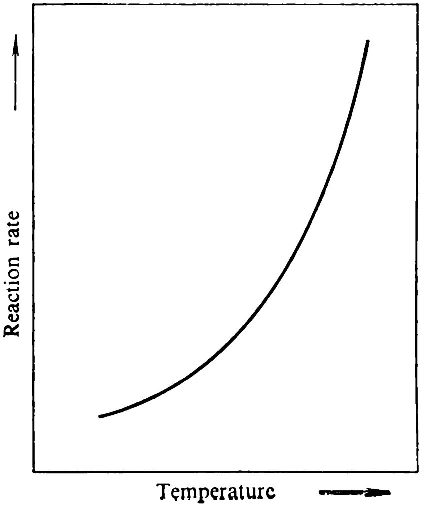


Fig. 15. **Temperature dependence of reaction rates**

The effect of temperature on the reaction rate is taken into account in the kinetic equation through the rate constant. The latter increases as the temperature rises and the reaction rate is therefore enhanced.

For complex reactions a temperature rise does not only increase their rates, but also changes their course. This can be illustrated by the concurrent reaction:

$$A \xrightarrow{k_{C_1}} B \tag{3.18a}$$

$$A \xrightarrow{k_{C_2}} D \tag{3.18b}$$

The rate constant for the first reaction is k_{C_1} and that for the second reaction, k_{C_2}. The kinetic equation for the first reaction is

$$r_1 = k_{C_1} C_A \tag{3.19a}$$

and for the second reaction:

$$r_2 = k_{C_2} C_A \tag{3.19b}$$

As the temperature rises, k_{C_1} and k_{C_2} increase and the rates of both reactions are therefore enhanced. But the rate constants may be increased differently. For example, if k_{C_1} increases to a greater extent than k_{C_2}, then a temperature rise accelerates the first reaction more than the second. As the temperature rises, this causes a greater yield of the product B (for a certain period of time) as compared with the yield of product D. The ratio of the contents of the final products B and D or the selectivity of the process will change. This circumstance should be remembered when attempting to increase the yield of a product in complex reactions.

The Effect of Catalysts. A chemical reaction may also be accelerated by using special substances called **catalysts** or **contacts**. Many chemical reactions cannot be carried out practically without using catalysts. Although it accelerates the reaction, the catalyst itself is not part of the final product and remains unchanged throughout the reaction system.

Catalysts not only may accelerate the chemical reaction, but they also direct the course of reactions. For example, depending on the catalyst used, different substances, such as hydrocarbons or alcohols, may be derived from carbon monoxide and hydrogen.

The Rate of Heterogeneous Processes. As compared with homogeneous processes, heterogeneous processes have some peculiar features. As an example, let us consider the absorption of sulphur dioxide with water. The process occurs in a heterogeneous gas-liquid system:

$$\underset{G}{SO_2} + \underset{L}{H_2O} \rightleftarrows \underset{L}{H_2SO_3} \qquad (3.20)$$

Figure 16 conventionally shows this process. Gaseous sulphur dioxide should be turned into a liquid, only then will it react chemically with water. The larger the contact surface of the reacting phases, the more SO_2 molecules will be turned into a liquid, and the more rapidly the chemical transformation will occur. Hence, the rate of the heterogeneous process is heavily dependent on the value of the phase contact surface, and the equation of the rate of a heterogeneous reaction necessarily includes the value of this surface (*F*).

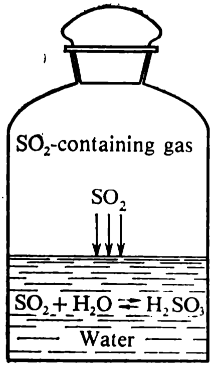


Fig. 16. Schematic of the process in the heterogeneous G—L system (absorption of sulphur dioxide with water)

As has been indicated above, sulphur dioxide should be turned into a liquid for a chemical reaction to occur. But this can be accomplished only under certain conditions for the following reason. When turned into the liquid phase, sulphur dioxide and water form sulphurous acid. This is a reversible reaction. Therefore, the sulphurous acid will decompose to form SO_2 and water, and a specific SO_2 concentration called the **equilibrium SO_2 concentration,** C_{eq}, will prevail above the surface of the liquid phase. Its value depends on the sulphurous acid concentration in the liquid. As SO_2 is absorbed and transformed into sulphurous acid, its concentration will increase in the liquid, and the equilibrium SO_2 concentration will therefore increase above the liquid. A moment may arrive when the equilibrium SO_2 concentration is equal to the SO_2 concentration throughout the gaseous phase volume, called the **actual SO_2 concentration,** C_{act}. The process of transferring of SO_2 from the gaseous to the liquid phase will stop, and no further chemical transformation will occur.

Thus, when conducting heterogeneous processes it is very important to know the difference between the actual concentration of the substance in the gaseous phase and its equilibrium concentration at the phase boundary. The difference in these concentrations is designated as ΔC and is called the **driving force of the process**:

$$\Delta C = C_{\text{act}} - C_{\text{eq}} \tag{3.21}$$

The greater the driving force of the heterogeneous process, the higher its rate. When the equilibrium concentration is equal to the actual concentration, the driving force is equal to zero, at this point the transfer of a substance from the gaseous phase to the liquid phase ceases and an equilibrium sets in.

In view of this, the equation of the rate of the heterogeneous process may be written

$$r_{\text{A}} = kF\Delta C \tag{3.22}$$

The quantity k is the **mass transfer coefficient**. (Like the rate constant for homogeneous processes, it specifies the rate of a process.) But the mass transfer coefficient is a more complex quantity; it depends not only on the chemical properties of the reactants, but also on physical properties, on the flow rates of reactants, the degree of agitation, and other factors.

Consideration of the kinetics of processes makes it possible to make an important conclusion that *to improve the reaction rate, it is essential*:

(1) to increase the initial concentrations of reactants (pressure for the reactions that occur in the gaseous phase);

(2) to raise temperatures;

(3) to employ catalysts;

(4) to increase the contact area between the substances that are in different phases.

All the measures listed above improve the most important parameter that characterizes the perfection of a process, i.e. chemical apparatus intensity. The higher the rate of chemical transformations, the greater the intensity of the apparatus. Therefore, all factors that accelerate chemical processes render them more intensive.

3.5 Choosing the Optimal Technological Conditions

After studying how the statics and kinetics of a process affect the choice of conditions for a process, one can find the most desirable (optimal) conditions from the technological point of view. Here is how the optimal temperature for a process is chosen in view of statics and kinetics.

Irreversible Reactions. The equilibrium of such reactions is practically completely shifted towards forming reaction products. As the temperature rises, the reaction rate increases, which is why *the temperature should be at a maximum for irreversible reactions.* The temperature rise is restricted by the instability of the material from which the apparatus has been manufactured or by decomposition of the reaction products and raw materials at high temperatures.

Reversible Endothermic Reactions. As the temperature rises, the equilibrium chemical yield and the reaction rate increase. Therefore, *reversible endothermic reactions should be conducted at maximum possible temperatures.*

Reversible Exothermic Reactions. As the temperature rises, the transformation rate increases, but the equilibrium chemical yield is reduced. Therefore, the process should be carried out in a range of temperatures where both the chemical yield and the rate are satisfactory. In practice, *reversible exothermic reactions should begin at high temperatures and the temperatures should then be lowered during the process.* At the beginning, high temperatures promote a high process rate. The main amount of the starting reactants undergo transformation. Lower temperatures at the end while causing a lower reaction rate allow a high chemical yield under equilibrium conditions.

However, technological conditions derived by theory are not always observed in practice. The economic efficiency of a process is very important. It is important not only to attain a high chemical yield at a high process rate, but also to spend minimum resources in manufacture of each unit of product, i.e. to reduce the specific consumption of raw materials, accessory materials, and energy. The technological conditions chosen so as to comply with these requirements may be considered to be economically rational.

3.6 Heterogeneous Systems

Heterogeneous processes are varied. Gases and liquids may be involved (adsorption, desorption, evaporation, condensation, and rectification illustrate these processes). Gases and solids are involved in adsorption and desorption, and liquids and solids in dissolution and crystallization.

In spite of the great variety of heterogeneous processes, they have a number of common features: all of them occur either on the contact surfaces of substances that are in different states of aggregation (at the phase boundary), or within the volume of a single phase, i.e. they always involve the transition of the substance from one (contributing) phase to the other (accepting) phase through an interface. All heterogeneous processes have a common feature i.e. to carry out such processes, it is essential that the concentration of the substance in the transfer phase is higher than the equilibrium concentration of this substance above the accepting phase, i.e. the driving force of the process should exist.

It is apparent from the equation for the rate of heterogeneous processes:

$$r = k \cdot F \cdot \Delta C \tag{3.22}$$

that, in order to accelerate such processes, the contact surface F between substances in different phases should be enlarged, the driving force (ΔC) of the process increased, and the mass transfer coefficient (k) improved.

To enlarge (develop) the contact surface F between substances F that are in different phases, the reacting phases are comminuted (dispersed). The process used to develop the phase contact surface depends on the type of heterogeneous system (G-L, G-S, L-S, L-L or S-S) and also on the conditions (pressure, temperature, and catalyst employed). The surface of the heavier phase, i.e. the solid phase in the G-S and L-S systems, and the liquid phase in the G-L systems, is generally enlarged. Let us recall the example of coal burned in air. A lump of coal burns comparatively slowly in air. If the contact surface of coal with air is enlarged by breaking the lump of coal into finer pieces, the combustion will improve significantly. The phase contact surface can also be enlarged by choosing a specific apparatus design.

To increase the driving force of the process (ΔC), which is the difference between the actual concentration of the substance C_{act} in the contributing phase and the equilibrium concentration C_{eq} above the accepting phase, the actual concentration of the substance is raised and the equilibrium concentration is lowered.

To raise C_{act}, concentrated raw materials may be used (for which purpose, the raw materials are subjected to beneficiation under industrial conditions). If a gaseous phase is involved in a reaction, the pressure should be increased, which is the same as increasing the concentration of the substance in the gaseous phase. For example, coal burns much faster in pure oxygen than in air, which contains as little as 21% oxygen.

To reduce C_{eq} one should know how the temperature affects the equilibrium and vary it accordingly (i.e. the temperature should be lowered in exothermic reactions and raised in endothermic ones). Also, the reaction products may be removed from the reaction volume to reduce C_{eq}. The reaction products are removed by condensation, selective absorption or adsorption from gas mixtures, and by decomposition, evaporation or adsorption from liquid mixtures.

Finally, to accelerate heterogeneous processes, *the mass transfer coefficient k should be improved.* Since it characterizes the rate of transfer of a substance from one phase to another, it is responsible for the rate of heterogeneous processes. To improve the mass transfer coefficient, one should know what factors affect it.

The mass transfer coefficient is a complex quantity, which depends both on the chemical properties of the reactants and on their physical properties, conditions of the process, and, in some cases, on the design of an apparatus. This relationship can be made more clear by another feature common to all heterogeneous processes: any heterogeneous process consists of a number of elementary stages. When coal is burned in air, carbon reacts with the oxygen molecules that are present directly at the surface of the coal, and carbon dioxide is formed here. The coal will continue to burn only if atmospheric oxygen is continuously fed to the coal surface, and the carbon dioxide is transferred to the gaseous phase. Thus, any heterogeneous process always includes at least three consecutive elementary stages:

(1) feeding the reactants to the interface (diffusion of the starting reactants);

(2) a chemical reaction;

(3) removing the reaction products from the interface (diffusion of the products).

The rates of these processes may prove to be unequal. In that case, the rate of the entire process will depend on the rate of the slowest stage, which will retard and limit the process. Any of the above-listed stages may be the slowest, and the nature of the entire process depends on this. If the chemical reaction proceeds at the slowest rate, however rapidly the reactants may be fed or the reaction products removed, the total process rate will be not greater than the chemical transformation rate.

A process in which the chemical reaction is the slowest stage is said to occur in the **kinetic region**. In such a process the mass transfer coefficient depends only on the reaction rate and does not depend on the diffusion rate. Therefore, to intensify a process that occurs in the kinetic region, the chemical reaction should be accelerated. This will improve the mass transfer coefficient and enhance the total process rate. In this case, some ways to enhance the chemical reaction rate are: temperatures should be raised, concentrations of the reactants increased, and catalysts employed.

A process in which diffusion occurs at the slowest rate of the three elementary stages of the heterogeneous process is said to occur in the **diffusion region**. However rapidly the reaction may proceed, if the reactants are fed slowly, the total process rate will also be low. In this case, the mass transfer coefficient depends on the rate of diffusion of the reactants. In order to enhance the total rate of a process that occurs in the diffusion region, measures should be taken to accelerate diffusion, i.e. to enhance the flow rates of the reacting phases, improve agitation of the reactants, and vary the conditions that affect viscosity, density, and other physical properties of the medium on which the diffusion rate depends.

When the chemical reaction and diffusion rates are approximately equal, the process is said to occur in the *transition region.* To accelerate this process, both the chemical reaction rate and the diffusion rate should be increased.

It is evident that depending on the region in which the heterogeneous process proceeds, various means are employed to accelerate it. In determining the region in which the process occurs, it should be borne in mind that the chemical reaction rate sharply increases as the temperature rises, whereas temperature does not have a substantial effect on the diffusion rate.

To determine the region in which the process occurs, it is carried out at various and ever increasing temperatures. The total process rate may be either enhanced or remain practically constant. As the temperature rises an increase in the total process rate occurs only for a process that proceeds in the kinetic region by increasing the rate of the slowest stage of the process, i.e. the chemical reaction. If a higher temperature does not practically increase the rate of the total process then the process depends on the diffusion rate rather than the chemical reaction rate (temperatures have almost no effect on the diffusion rate); the process proceeds in the diffusion region.

Thus, **to enhance the rate of homogeneous processes, it is essential**:

(1) to increase the phase contact surface (irrespective of the region in which the process proceeds);

(2) to increase the driving force of the process (irrespective of the region in which the process occurs) by:

(a) increasing the actual concentration of a substance in the contributing phase (pressure in the gaseous phase);

(b) taking measures to lower the equilibrium concentration of the substance in the accepting phase;

(3) to improve the mass transfer coefficient by:

(a) raising temperatures, concentrations of the reactants and employing catalysts, etc., if the process proceeds in the kinetic region so as to increase the chemical reaction rate;

(b) enhancing the flow rates of the reacting phases, improving agitation, etc., if the process proceeds in the diffusion region, to increase diffusion.

Apparatus Employed in Heterogeneous Processes. Reactors employed to carry out a heterogeneous process should be constructed so as to maintain a large contact surface between the substances in different states of aggregation. Attempts should also be made to intensify agitation of the reactants; this results in renewing the phase contact surface and improving the diffusion conditions.

Reactors in which the G-S and L-S systems are treated may be subdivided into four groups.

Filter or stationary bed apparatus (Fig. 17). A stationary bed *2* of solid particles rests on grid *1*, and a gas or liquid stream is passed through this bed. Apparatus of this type are simple in design; however, they are not suitable for renewing the phase contact surface; nor can a highly ground solid material be used or high gas flow rates, since this increases the power consumption for feeding a gas or a liquid through the solid material bed. In a filter bed apparatus, it is somewhat difficult to remove or supply the heat required for carrying out reactions.

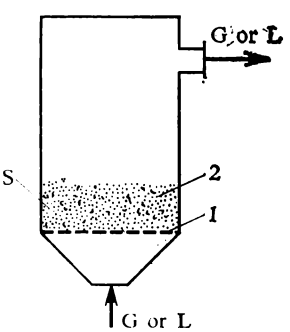


Fig. 17. Filter or stationary-bed reactor

1—grid; *2*—bed of solid particles

Apparatus with stirrers (Fig. 18). Figure 18*a* shows the diagram of an apparatus with a stirrer for L-S systems. In a number of cases, a few of these are connected in series to form a cascade of reactors. Figure 18*b* shows the diagram of an apparatus for the treatment of G-S systems. It is essentially a vertical cylinder *1* whose interior accommodates horizontal roofs *3*. The centre of the apparatus mounts shaft *4*. Paddles *5* with blades (teeth) fitted on them are located horizontally on the shaft. During operation the shaft with the paddles rotates, not merely stirring the solid material on the roofs, but also moving it from the upper roof to the lower roof through the holes in roofs *6*. The gas is fed from the bottom and directed in counterflow with respect to the solid material. The resulting gaseous reaction products are removed from the apparatus at the top, and the solid reaction products from the bottom. This type of apparatus is employed, for example, in the sulphuric acid industry for roasting pyrite (mechanical furnaces).

Apparatus with stirrers allow a continuous renewal of the phase contact surface, which accelerates diffusion processes. However, these apparatus, especially those for the G-S system, are complicated in design and do not convert the starting material to a great extent.

Apparatus in which phases are reacted in a stream (Fig. 19). Apparatus for a G-S system are essentially hollow chambers.

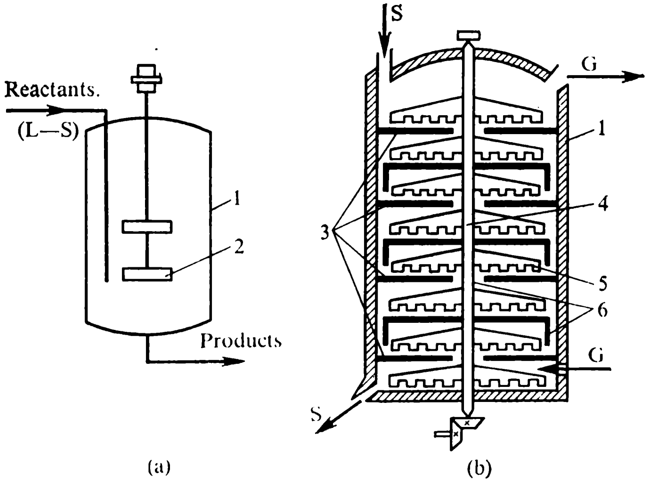


Fig. 18. Stirred reactors

(*a*) for L-S system; (*b*) for G-S systems; *1*—cylinder; *2*—stirrer; *3*—roofs; *4*—shaft; *5*—paddles; *6*—holes in roofs

The gaseous reactant is fed into these chambers through pneumatic nozzles spraying a finely divided solid material. The gas and the solid material react chemically in the stream. The solid products are separated from the gaseous ones by gravity. Apparatus of this type are simple in design. The reaction proceeds at a high rate in the stream owing to the development of the phase contact surface. This causes the reaction to occur very intensely. The substantial disadvantage of an apparatus of this type is that solid particles are removed by a gas stream, thus contaminating the gaseous reaction products and losing solid reaction products.

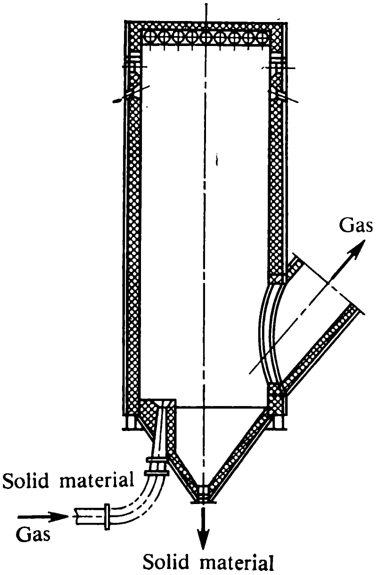


Fig. 19. Reactor for phase interacting in a stream for G-S systems

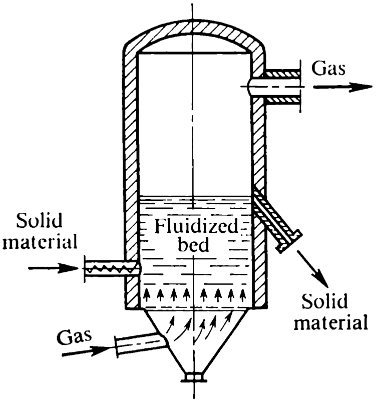


Fig. 20. Fluidized bed reactor

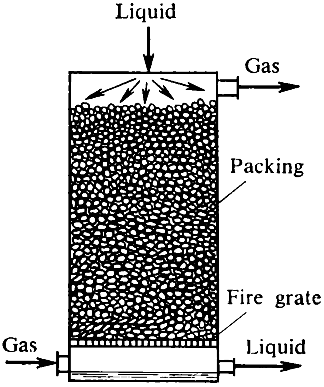


Fig. 21. Packed tower

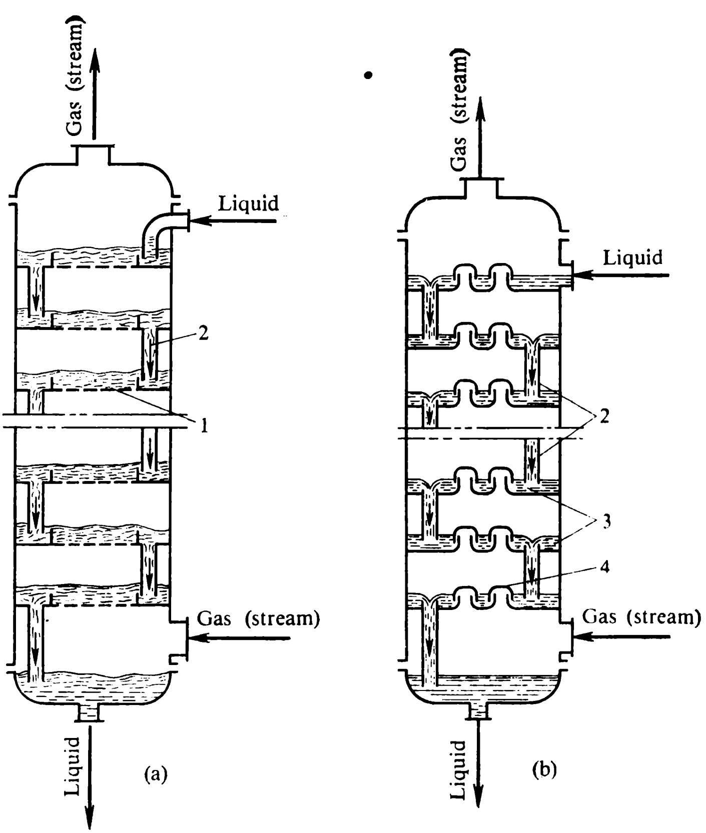


Fig. 22. Bubble columns; perforated-tray column (*a*) and bubble-cap column (*b*)

1—sieve tray; *2*—overflow tube; *3*—bubble-cap tray; *4*—cap

Fluidized bed apparatus (Fig. 20). A fluidized bed is formed in the apparatus of this type when a gas or a liquid is passed upwards through a solid material bed at such a rate that the particles go into suspension, float, and pulse in a gas or liquid stream, but stay within the boundaries of the suspended bed. The solid material is continuously fed to a grid under which air is also fed at a rate that allows transfer of the particles to the fluidized state. The temperature of the fluidized bed is constant; it may be controlled in the bed by installing heat exchangers. Fluidized beds are especially useful for processes whose rate is determined by the diffusion resistance in the gaseous phase. Under fluidization conditions this resistance is reduced tens and sometimes hundreds of times, thus enhancing the process rate, accordingly.

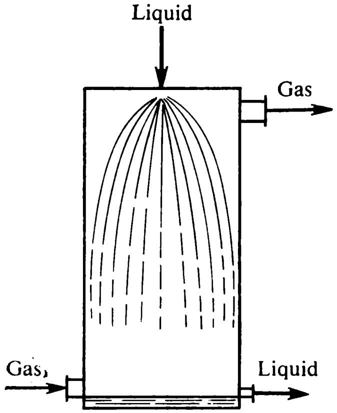


Fig. 23. Water spray tower

Apparatus in which processes proceed in the G-L systems are subdivided into four groups.

Surface and film absorbers are apparatus in which a gas passes above the surface of the liquid which is either at rest or flowing slowly. The surface of the liquid acts as a mass transfer surface. In film absorbers, the gas and the liquid make contact on the surface of the film which runs off along a vertical surface, which is essentially a pipe or plates.

Packed apparatus (Fig. 21) are columns filled with a packing of various types. The liquid is fed onto the packing from the top and runs downwards over the packing to form a film of liquid on its surface. The gas is then usually fed into a tower or a column from the bottom in countercurrent to the liquid that is running down. The gas makes contact with the liquid on the wetted packing surface.

Bubblers are columns in which the gas contacts the liquid when gas pockets pass through a layer of the liquid. To break the gas stream into finer pockets, sieve trays (grids) (Fig. 22*a*) or bubble-cap trays (Fig. 22*b*) are installed in the apparatus.

Apparatus with a liquid sprayed or sprinkled to a gas volume (stream) (Fig. 23).

In L-L (immiscible liquids) systems, the phase contact surface is developed by dispersing one liquid phase in the form of drops into the other in a spray, packed, tray-type, or other type of apparatus.

S-S systems use agitation by mechanical and pneumatic stirrers and rotary drums. A rotary hollow drum (Fig. 24) is installed at a slight angle. The drum is then set into rotation from the drive by a gear wheel fitted to the drum. Raw material is fed into the drum through a feeder. As the drum rotates, the raw material moves towards the discharge opening. The apparatus is heated by flue gases moving in countercurrent to the reactants or flowing around the apparatus externally.

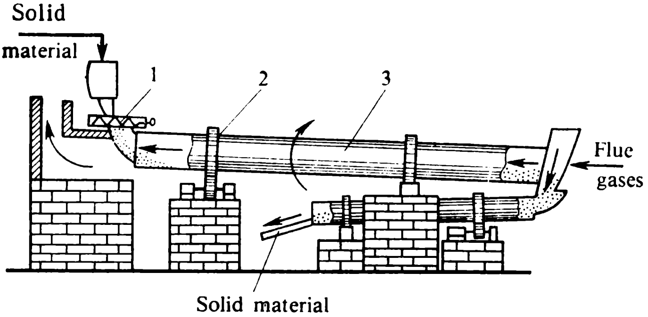


Fig. 24. Rotary drum

1—feeder; *2*—gear wheel; *3*—drum

3.7 Catalytic Processes

Many reactions proceed very slowly. However, they may be accelerated by adding **catalysts**. These are substances whose presence enables the reaction to proceed at a high rate, while the catalysts themselves remain unchanged.

A process whose rate is enhanced by catalysts is called a **catalytic process**. Catalytic processes have found exceedingly wide industrial applications; at present about 90% of industrial processes are catalytic. The manufacture of hydrogen, ammonia, phenol formaldehyde resins, and many other products relate to catalytic processes.

It should be noted that catalysts are predominantly used to accelerate reactions. Processes in which catalysts are used to accelerate reactions are called **positive catalysis.** There are cases when catalysts are used to retard processes (e.g. oxidative processes). This is called **negative catalysis.**

A process in which the catalyst and the reactants are in the same state of aggregation (e.g. the reactants and the catalyst are liquid or gaseous) is called **homogeneous catalysis.** When the reactants and the catalyst are in different states of aggregation (e.g. the reactants are gaseous and the catalyst is solid, or the reactants are gaseous and the catalyst is liquid), the process is called **heterogeneous catalysis.**

Various catalysts accelerate the same process in varying degrees. *Catalyst activity is the measure of the accelerating action of a catalyst in a given reaction.* The higher the catalyst activity, the more it accelerates the reaction rate, and the reaction may therefore be carried out in the presence of a catalyst at a high rate even at low temperatures.

The minimum temperature at which a catalytic process can proceed at a rate sufficient to be useful industrially is called the **catalyst ignition temperature.**

As has been mentioned, catalysts do not undergo any changes after the reaction, i.e. their properties and composition remain unchanged. In actual conditions, however, during the operation the catalyst gradually becomes incapable of accelerating reactions. In other words, catalyst activity becomes lower and even a complete loss of activity may take place, i.e. the catalyst becomes **deactivated.** Deactivation of the catalyst is caused by its "poisoning" with some compounds present in the reactants that enter into reactions. Such substances are called **contact poisons.** Hence, to make catalysts active for a long period of time, the reactants should be thoroughly cleaned from contact poisons.

Homogeneous catalytic processes. The homogeneous catalytic process may schematically be presented as follows. Let the compounds A and B react in the gaseous phase to form the product AB:

$$A + B = AB \tag{3.23}$$

In order to accelerate the reaction, it is carried out in the presence of the catalyst K. This causes the process to proceed in a different manner, namely, compound A reacts with catalyst K:

$$A + K = AK \tag{3.24}$$

to form compound AK which, in turn, reacts with compound B:

$$AK + B = AB + K \tag{3.25}$$

Thus, the course of the reaction changed: reaction (3.24) produced the intermediate compound AK and reaction (3.25) produced the compound AB, and the catalyst remained unchanged. The rate of reactions (3.24) and (3.25) is much higher than the rate of reaction (3.23) and therefore, due to the presence of the catalyst, the compound AB is formed at a high rate.

The rate of a homogeneous catalytic process increases by increasing the catalyst activity, raising the temperature, increasing the concentrations of the reactants and the catalyst; the rate sometimes increases during agitation of the reactants.

Heterogeneous catalytic processes. Heterogeneous catalytic processes have found wide application in industry. Solid catalyst processes have been employed very extensively to carry out reactions between gaseous substances, for example, between hydrogen and nitrogen to form ammonia, and sulphur dioxide and oxygen to form sulphur trioxide.

In the presence of solid catalysts, the reactants are first diffused to the catalyst surface, they then penetrate into the catalyst pores and are deposited, i.e. adsorbed in its surface. The reaction occurs on the catalyst surface. The resultant reaction products are diffused through the pores of the catalyst to its surface and from the catalyst surface into the volume that surrounds the catalyst. The rates of individual stages of such a process are different. As is the case with heterogeneous non-catalytic processes, it is necessary to determine the slowest stage (the limiting stage) of the heterogeneous catalytic process, the stage on which its overall rate depends. If the diffusion stage proves to be the slowest, the process is said to be proceeding in the *diffusion region*. This process can be accelerated by increasing the diffusion rate. To this end, it is desirable to agitate the reactants to accelerate diffusion, or to prepare a catalyst having large pores that facilitate penetration by the gases within the catalyst particle.

If the process rate is determined by the chemical reaction rate, the process is said to be proceeding in the *kinetic* *region*; the temperature should be raised and the concentration of reactants increased to make the process more intensive.

When adsorption is the slowest stage, it is desirable to increase the concentration of reactants and improve catalyst porosity.

The Process Parameters. To ensure that the reaction is carried out completely, it is essential that the reactants should be in contact with the catalyst for a sufficient period of time. This period is called the **contact time.** The duration of contact with the catalyst is determined by the **volumetric rate** which shows what amount of gas volumes per cubic metre (at 0 °C and at a pressure of 760 mmHg) passes in one hour through 1 m^3 of the catalyst.

The more complete the reaction on the catalyst, the higher the **catalyst activity** or **intensity.** This is the amount of the product, in kg, obtained from 1 m^3 of the catalyst in one hour. It is always necessary to carry out the process under industrial conditions so that catalyst activity may be as high as possible.

Industrial Catalysts. These mixtures are mostly called **contact masses.** The contact masses include substances such as catalysts proper, carriers, and promoters.

Catalysts are metal oxides, such as iron, aluminium, and cobalt oxides; iron, copper, and other metals, some salts; mercury chloride, alumosilicates, and other compounds.

Carriers are pumice, asbestos, kaolin, coal, and other highly porous substances which improve the porosity of the catalyst, rendering it strong and reducing its cost.

Promoters improve catalyst activity. They include, for example, oxides of potassium, calcium, and aluminium.

Apparatus Employed in Heterogeneous Catalytic Processes. To carry out heterogeneous catalytic processes, various types of reactors called **catalytic reactors** are used.

Cylindrically shaped metal *capacity-type contact reactors* (Fig. 25) have grid *1* on which catalyst bed *2* rests. The gases pass up through the catalytic reactor, or down. Apparatus of this type are simple in design and are used, for example, in the petroleum refining industry.

Shelf-type catalytic reactors (Fig. 26) have a number of shelves *2* on which catalyst *1* rests. Heat exchangers *3* are located between the shelves. These apparatus are generally used to carry out exothermic reactions. Prior to penetration into the catalyst while resting on the upper shelf, the reacting gases pass, in succession, through the intertube space of heat exchangers *3* and become heated. The exothermic reaction occurs on the upper shelf, and the gas temperature rises. The hot gases are admitted into the tubes of heat exchangers *3* where the gases cool, since cooler gases are moving in the intertube space of the heat exchangers. From the heat exchanger tubes, the gas mixture penetrates the next catalyst bed and then onto the next heat exchanger to cool. After passing through all the catalyst beds and the heat exchangers, the gas mixture is withdrawn from the reactor.

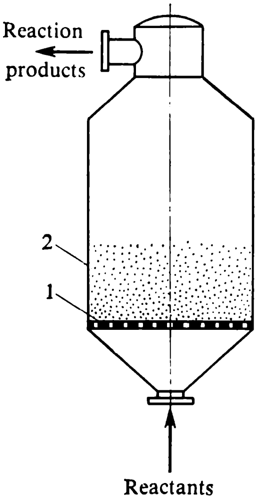


Fig. 25. Capacity-type catalytic reactor

1—grid; *2*—catalyst bed

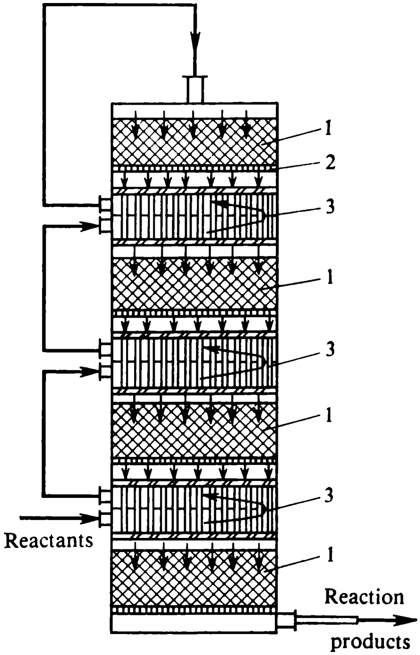


Fig. 26. Shelf-type catalytic reactor

1—catalyst; *2*—shelf; *3*—heat exchangers

Thus, a specific temperature is maintained in each bed of the catalytic mass and the reaction heat is used for catalytic purposes. Apparatus of this type are used in the oxidation of sulphur dioxide to sulphur trioxide, in the synthesis of ammonia from nitrogen and hydrogen and many other processes.

Tubular catalytic reactors (Fig. 27) are similar in construction to tubular heat exchangers. A catalyst rests on tubes along which the reacting gases are passed. If the reaction absorbs heat, heating gases are fed into intertube space to maintain the desired temperature in the tubes.

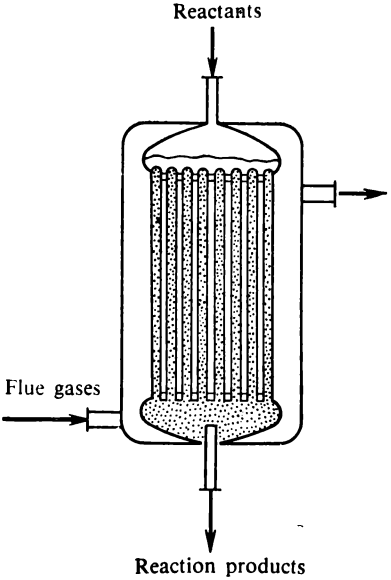


Fig. 27. Tubular catalytic reactor

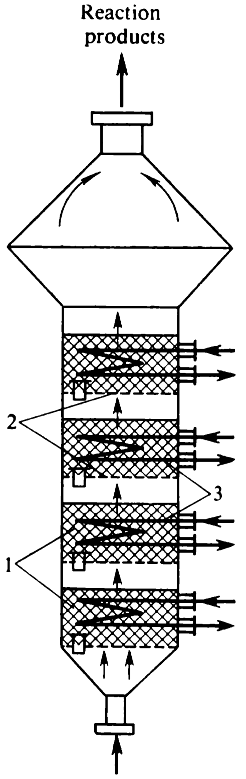


Fig. 28. Fluidized-bed catalytic reactor

1—catalyst; 2—shelves; 3—coils

Tubular catalytic reactors are employed in the manufacture of nitric acid and other industries.

Fluidized bed apparatus (Fig. 28) have a number of shelves *2* on which finely grained catalyst *1* rests. Gaseous reactants are fed at a high rate from the bottom of the reactor. While passing through the catalyst, these reactants bring the latter to the "fluidization" state, i.e. the particles rise and become intermixed. Externally, the bed resembles a boiling liquid. A reaction occurs in each "fluidized" catalyst bed. The reaction mixture is withdrawn from the top of the apparatus. Removal or supply of heat may be accomplished by coil pipes *3* immersed in the catalyst bed.

Apparatus of this type are simple in construction and are highly efficient. They are employed in the manufacture of sulphuric acid, in petroleum refining, and other industries.

Mobile catalyst apparatus (Fig. 29) are used when the catalyst rapidly loses its activity during a process and its catalytic properties must be restored. The reactor consists of two parts. Catalytic reactor *1* is located at the top and regenerator *2* at the bottom. The catalyst is admitted from the top of the catalytic reactor and is continuously moving downwards. The reactants are moving in counterflow to the catalyst.

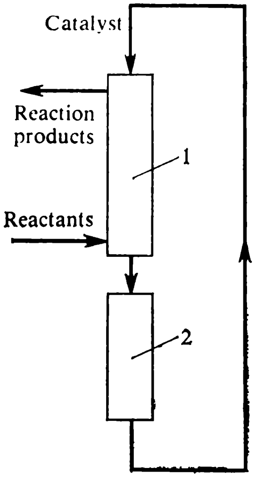


Fig. 29. Schematic of operation of moving-bed catalytic reactor

1—catalytic reactor; *2*—regenerator

The reaction products are withdrawn from the top of the apparatus. From the catalytic reactor the deactivated catalyst is admitted into regenerator *2* in which it also moves downwards. The catalyst whose activity has been restored in the regenerator is again fed to the top of the catalytic reactor.

Catalytic reactors of this type have been employed in petroleum refining and in processing petroleum products.

3.8 Material and Energy Balances

Calculations are made when quantitatively estimating and analysing processes, when comparing various manufacturing processes, and also when choosing reaction or other apparatus. Material and energy balances are drawn up to demonstrate the quantitative changes that occur in the process. These balances enable one to determine process parameters, like the raw material and power consumption, the amount of the resulting waste, the quality of products being manufactured, the overall dimensions of apparatus, and transport facilities.

The material balance is based on the law of mass conservation. For a technological process, it implies that the mass of the substances to be processed, i.e. **input** $G_{\mathrm{inp.}}$ is equal to the mass of the resulting substances, i.e. **output** $G_{\mathrm{out.}}$:

$$G_{\mathrm{inp.}} = G_{\mathrm{out.}} \tag{3.26}$$

The material balance is drawn up according to the equation for the overall reaction taking into account the concurrent and side reactions.

In industry, raw materials of complex composition, as opposed to pure substances, have to be handled. Therefore, the mass of the basic components and that of impurities are compared (balanced), according to analysis data, with the mass of the basic product being manufactured, by-products, and industrial waste.

The mass of a substance is often determined separately for solid, liquid, and gaseous phases. Thus, the material balance equation may be expressed as follows:

$$G_{\mathrm{s}} + G_{\mathrm{l}} + G_{\mathrm{g}} = G'_{\mathrm{s}} + G'_{\mathrm{l}} + G'_{\mathrm{g}} \tag{3.27}$$

where G_{s}, G_{l} and G_{g} are the masses of solid, liquid, and gaseous materials, respectively and G'_{s}, G'_{l}, and G'_{g} are the masses of the manufactured products.

Practically, calculation does not always involve all three phases. There may be several substances in a single phase, which makes Eq. (3.27) either simpler or more complex.

The material balance is made up in terms of the raw material consumption and the manufacture of by-products per unit of the basic product (kg/t, kg/mole) or per unit time (hour, day, month).

Given below is an example illustrating the balance of sulphur pyrite calcination. Sulphur pyrite, the valuable constituent of which is iron disulphide (FeS_2), is oxidized in a calcining kiln with atmospheric oxygen according to the following equation:

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2 + Q \tag{3.28}$$

To draw up the material balance, it is necessary to take into account the amount of all the substances fed to the calcination kiln (the input items) and also those withdrawn from the kiln (the output items), and tabulate the data. The input items in the process under review include pyrite, air, and also moisture which is always present.

The output items include cinder, derived from the reaction and containing predominantly Fe_2O_3, and also the kiln gas which is essentially a gas mixture composed of SO_2, SO_3, O_2, N_2, and water vapours (Table 1).

TABLE 1. **The Material Balance for Pyrite Calcining Kilns (Capacity 20 t/h H_2SO_4)**

Input	Amount		Output	Amount	
	kg	m^3		kg	m^3
Pyrite	18 020	—	Cinder	13 560	—
Moisture with pyrite	560	—	Roaster gas		
			SO_2	13 780	4 700
Dry air	70 250	54 400	SO_3	940	260
Moisture with air	510	634	O_2	6 360	4 440
			N_2	53 700	49 920
			H_2O	1 060	1 320
Total	89 400	55 034	Total	89 400	53 600

To calculate all these values, it is essential to know the stoichiometric equation that defines the reaction, kiln capacity, the composition of products being processed, and also the degree of utilization of the initial material. The material balance is based on such data and is shown in Table 1. All the values are calculated for one-hour kiln operation, i.e. the balance has been drawn up per unit time.

The energy balance is based on the law of energy conservation. The *heat balance* is mostly drawn up for chemical technological processes. When applied to the heat balance, the law of energy conservation may be formulated as follows: the amount of heat supplied for the technological operation, i.e. the heat input $Q_{\text{inp.}}$ is equal to the heat output $Q_{\text{out.}}$ for the same operation:

$$Q_{\text{inp.}} = Q_{\text{out.}} \tag{3.29}$$

The heat balance is based on the material balance data, the heat effects of chemical reactions and physical transformations occurring in the apparatus. Any external heat supply or heat removal together with the reaction products and through the apparatus walls should be taken into account. Hence, the heat balance equation may be expressed as follows:

$$\begin{aligned} Q_s + Q_g + Q_l + Q_r + Q_{ph} + Q_{loss} &= \\ &= Q'_s + Q'_g + Q'_l + Q'_r + Q'_{ph} + Q'_{loss} \end{aligned} \tag{3.30}$$

where Q_s, Q_l, Q_g are the heats introduced together with solid, liquid, and gaseous products admitted into the apparatus; Q'_s, Q'_l, and Q'_g are the heats of the products removed; Q_r and Q'_r are the heats of exothermic and endothermic reactions, respectively; Q_{ph} and Q'_{ph} are the heats of physical processes occurring with evolution and absorption of heat, respectively; Q_{loss} is the heat supplied externally; and Q'_{loss} is the heat lost to the environment and heat removal through coolers located within the apparatus.

REVIEW QUESTIONS

1. What are the basic requirements that any chemical technological process should meet?
2. What process conditions are called optimal?
3. What basic stages are chemical technological processes made up of?

4. By what features are chemical reactions classified? What basic types of chemical reactions do you know? Give examples.

5. What processes are called reversible and irreversible? Give examples.

6. What systems are called homogeneous and heterogeneous? Give examples of two homogeneous and two heterogeneous reactions which have not been mentioned in the text.

7. What processes is the Le Chatelier principle applicable to?

8. What factors affect the state of equilibrium?

9. What effect do temperatures have on reversible exothermic and endothermic processes?

10. What effect do pressures have on the equilibrium of reversible processes occurring in the gaseous phase in a reduced volume?

11. What effects do the concentrations of the initial substances have on the equilibrium shift?

12. What basic factors does the chemical process rate depend on?

13. Explain why ammonia is manufactured under industrial conditions at a relatively high temperature (about 550 °C), although the synthesis of ammonia from nitrogen and hydrogen is an exothermic reaction.

14. A reaction of hydrogen with chlorine to form hydrogen chloride occurs as follows:

$$\underset{\mathrm{G}}{H_2} + \underset{\mathrm{G}}{Cl_2} \rightleftharpoons \underset{\mathrm{G}}{2HCl} + 185\ \mathrm{kJ}$$

What three conclusions can be made from the equation of this reaction?

15. How can the equilibrium of reversible exothermic reactions be shifted when synthesizing ammonia and converting carbon monoxide?

16. Why are attempts made to create a large surface for a solid substance when carrying out a reaction between a solid substance and a gas or a liquid under industrial conditions?

17. How is the phase contact surface increased in the heterogeneous G-S, L-S, and G-L systems?

18. What stages are heterogeneous processes made up of?

19. How is the rate of heterogeneous processes occurring in the kinetic and diffusion regions increased?

20. What is the best temperature condition for carrying out reversible exothermic reactions, reversible endothermic reactions, and irreversible reactions?

21. What are catalysts used for?

22. What is catalyst "poisoning"?

23. Consider the following reaction:

$$4HCl + \underset{G}{O_2} \rightleftarrows \underset{G}{2H_2O} + \underset{G}{2Cl_2} + 113\ kJ$$

What effect on the equilibrium Cl_2 concentration will be exerted by:

(a) a higher temperature in the reaction vessel,
(b) a reduced total pressure,
(c) a higher O_2 concentration?

Give reasons to prove your answer.

Chapter 4

TYPICAL METHODS FOR THE ORGANIZATION OF TECHNOLOGICAL PROCESSES

The chemical industry manufactures thousands of products which possess diverse properties and are applicable in many industries of the national economy.

Despite the great variety of chemical products, process conditions, reaction and non-reaction apparatus employed, chemical technological processes have general regularities which determine the desired conditions for a process. There are also some common features in the way processes are organized.

The Basic Stages. The manufacture of chemical products includes a number of physical and chemical processes. The raw material is prepared for processing, the reactants are transported (they are moved from apparatus to apparatus), chemical reactions are carried out, the resulting products are separated, they are stored and packed, and so on. A sequential description and graphic representation of all the stages for processing the initial substances into manufactured products and the apparatus employed for this purpose are called **flow diagrams.**

Despite the fact that chemical technological processes and flow diagrams are complex, typical flow diagrams may be singled out which are most frequently employed under industrial conditions.

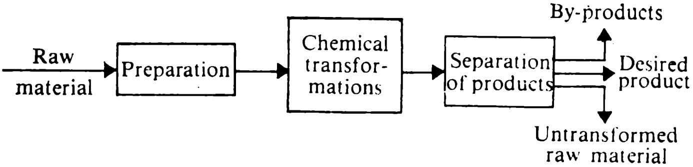


Fig. 30. Open-chain diagram

Chemical technological processes are generally comprised of three stages, namely, preparation of raw materials, chemical transformations, and the recovery of the desired products (Fig. 30).

Preparation of raw materials. The requirements for raw materials depend on the type of chemical industry. In some cases, it is convenient to process raw materials in solid form, in other cases, in solution, melted or gas form. For some chemical technological operations, it is more desirable to process solid raw materials in the form of small-sized lumps, and for other operations, in the form of large-sized lumps. Often the raw materials are processed only after the valuable component in the raw material is concentrated (after beneficiation of the raw material).

The first stage of a chemical technological process is to prepare raw materials. The raw materials must be processed in such a way that their composition and properties meet the requirements of a given industry and assure a high rate of chemical transformations. For many types of raw materials, the requirements for them are established by the USSR State Standards or Specifications.

Raw materials are prepared by grinding, concentrating, drying, removing dust from gases, and so on. The operations used to prepare raw materials depend on the specific requirements of the subsequent stage, the stage of chemical transformations.

Chemical transformations. At this stage, the raw material components enter into a chemical reaction to form new substances.

The basic regularities of chemical processes dealt with earlier allow determination of the conditions that render processes highly intensive.

In most cases, pure products are not obtained as a result of chemical transformations. They may be contaminated with partially unreacted raw materials; if a plurality of products, rather than a single product, results from the reaction, the desired product will be mixed with a number of by-products that are not used in a given process. The desired product therefore must be separated from the mixture of products.

Separation of the desired products is accomplished by rectification, absorption, adsorption, crystallization, evaporation, etc.

Rectification may be used to separate homogeneous mixtures of liquids that boil at different temperatures. If, for example, a liquid composed of ethanol and water is heated and partially evaporated, the alcohol will evaporate more readily than water, since the former boils at a lower temperature. Therefore, there will be more alcohol in the vapours than in the initial liquid mixture. If these vapours are to be separated, again cooled and transformed into a liquid (to be condensed), the alcohol content in water will also be higher than in the initial mixture. Repetition of these operations (evaporation and condensation) using an alcohol-rich liquid yields a product with a still higher alcohol content. This is the process that occurs during rectification when partial evaporation of a mixture and condensation of its vapours are repeated many times in a fractionating column where the liquid is heated.

Absorption of a gas by a liquid is employed to separate gas mixtures that are composed of gases absorbed by a liquid in varying degrees. This process is related to the transition of a substance from the gaseous to the liquid phase. The process is carried out in absorption columns in which the gas mixture contacts a liquid. The liquid is selected so that it can absorb only those gases that are to be recovered from the mixture. The remaining gases, which cannot be absorbed by the chosen liquid, should be removed from the column. For example, if carbon dioxide is to be removed from a nitrogen-hydrogen mixture, the mixture is passed through a column into which water is fed. Only carbon dioxide is dissolved in water, and the mixture composed of nitrogen and hydrogen, and, cleared of carbon dioxide, leaves the column.

The process in which a solid rather than a liquid absorber is used to separate gas or liquid mixtures is called *adsorption.* This separation process is defined as the transition of a substance from the gaseous or liquid phase to the solid phase.

Crystallization may be used to separate a substance from solutions or melts. Conditions are selected that reduce the solubility of a substance and the substance is recovered from the liquid phase in the form of crystals.

During *evaporation* substances are separated due to the transition of one substance from a liquid to the vapour phase.

4.1 Flow Diagrams of Chemical Technological Processes

A successive description and graphic representation of all the stages for processing the initial substances into manufactured products, and the apparatus employed for this purpose are called production **flow diagrams.** They give an idea of how the individual elements of the system are united. There are three types of diagrams: functional, flow, and structural (block) diagrams.

The functional diagram shows the links between the individual stages of the process, each performing its definite function. Figure 31 is a functional diagram of the manufacture of ammonia. This diagram does not only show the essence of the individual stages in the manufacture of ammonia, but, what is very significant, describes the links between them.

The flow diagram shows the individual elements of the technological process, **methods for linking these elements,**

and the succession of the individual operations. To this end, each element incorporated in the flow diagram (an assembly or an apparatus) is appropriately represented. The links between the apparatus are depicted by arrows. The flow diagram for ammonia synthesis shown in Fig. 32 serves as an example.

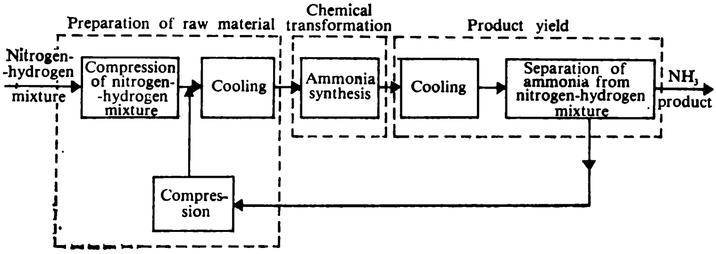

Preparation of raw material
Chemical transformation
Product yield
Nitrogen--hydrogen mixture
Compression of nitrogen--hydrogen mixture
Cooling
Ammonia synthesis
Cooling
Separation of ammonia from nitrogen-hydrogen mixture
NH_3 product
Compression

Fig. 31. Functional diagram of ammonia synthesis

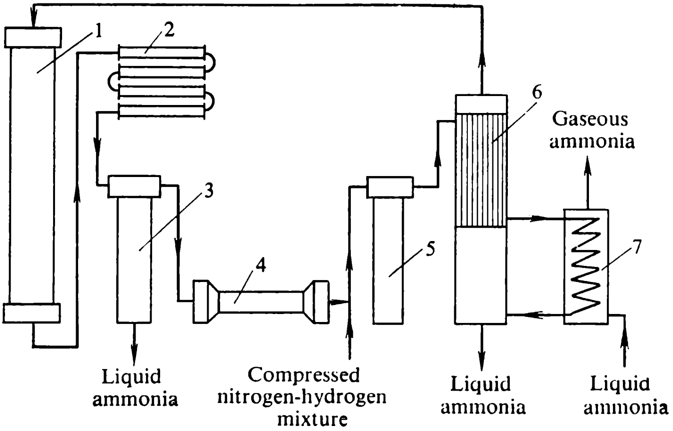


Fig. 32. Flow diagram of ammonia synthesis

1—ammonia synthesis column; *2*—water condenser; *3*—separator; *4*—circulating pump; *5*—filter; *6*—condensation column; *7*—evaporator

In a number of cases, the flow diagram provides data on the substances involved in the process, and on the parameters of the process.

Flow diagrams have found wide application. They are employed in developing, designing, and operating chemical technological processes.

The structural (block) diagram is typical in that the individual process elements, unlike the flow diagram, are depicted as blocks. This diagram depicted by arrows shows the links between the blocks. The arrows indicate the direction of the material and power flows (Fig. 33).

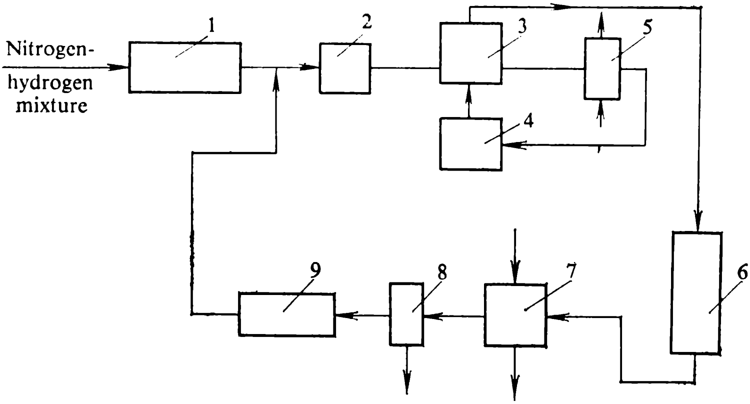


Fig. 33. Structural diagram of ammonia synthesis

1—compressor; *2*—filter; *3*—upper portion of condensation column (heat exchanger); *4*—bottom portion of condensation column (separator); *5*—ammonia cooler; *6*—synthesis column; *7*—water cooler; *8*—separator; *9*—circulating compressor

4.2 Technological Links

Examination of the diagrams indicates that there is a specific interaction between the individual elements of the process. This interaction is maintained by technological links. There may be series, series by-pass, parallel, reverse (recycle), and cross links.

The series technological link is typical in that the raw material is processed by passing through each apparatus one by one. Such a system may include several apparatus in series operating in each stage of the process. For example, the diagram is comprised of several series reactors (Fig. 34). The degree of conversion attained in the output of the last reactor is the same as that in a single reactor whose length is equal to the total length of all the reactors connected in series.

The parallel technological links (Fig. 35) are typified by the continuous flow of the raw material being separated with only part of the raw material admitted to each of the apparatus. If the height of the apparatus is the same, i.e. the raw material residence time is the same, the same degree of conversion is attained. Processed products are removed from each apparatus and then combined to form a single common flow.

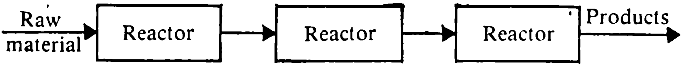


Fig. 34. Consecutive technological link

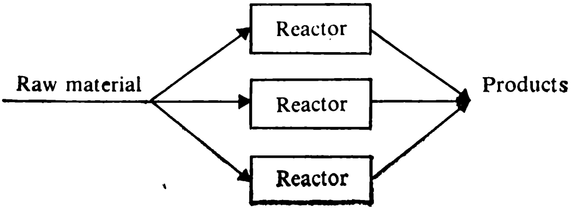


Fig. 35. Parallel technological link

The series by-pass technological link is depicted in Fig. 36. It is apparent from this diagram that all the apparatus are connected in series. However, in this case, the raw material to be processed is separated into two flows. One flow passes through all the stages in series. The other flow is mixed with the products withdrawn from the first stage, whereupon the resulting mixture is directed to the next stage. If, for example, preparation of the raw material includes heating the reaction mixture, the introduction of a cold by-pass flow into this mixture makes it possible, prior to the chemical transformation stage, to control the temperature needed to carry out the chemical reactions.

In all of these cases the raw material is processed by passing it through each apparatus of each process stage in succession. It passes from one apparatus to another and is admitted to each apparatus only once. Such flow diagrams are called **open-chain diagrams.**

The reverse technological link (recycle) is essential if one pass of the starting reactants through the reaction apparatus cannot provide a high degree of conversion. A reversible exothermic reaction serves as an example. When this reaction is carried out at elevated temperatures, there is incomplete transformation of the raw material into the reaction products.

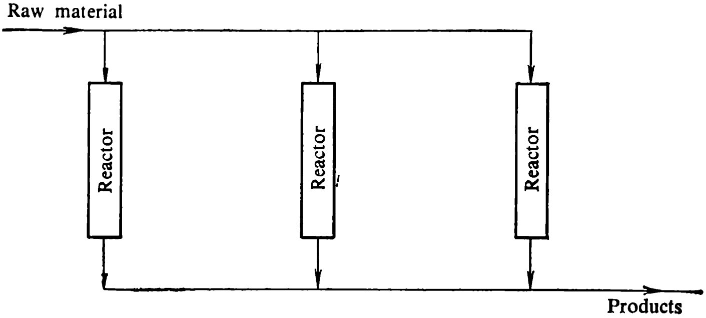


Fig. 36. Consecutive by-pass technological link

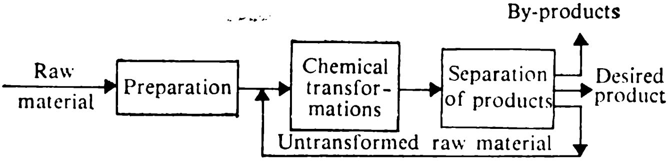


Fig. 37. Recycle technological link

Therefore, to improve the degree of conversion of the initial substances, the production is organized on a cyclic (circulation) diagram (Fig. 37). After the reactants have passed through the apparatus of the stage of chemical transformations, the resulting product is separated from the untransformed raw material. This raw material is then mixed with fresh raw material and recycled for repeated chemical treatment.

Diagrams according to which the whole of the unreacted raw material is fed for repeated processing are called *diagrams with full recirculation*. In *diagrams with partial recirculation*, only part of the unreacted raw material is recycled to the reactor.

Cyclic diagrams are widely employed in the synthesis of ammonia, methanol, and other compounds. Plants employing a cyclic diagram are more compact, they include fewer apparatus and process the initial substances into products to a fuller extent as compared with open-chain diagrams. Circulation is also used when some adjuvant is to be recycled into the process. This adjuvant is isolated at the end of the process and used at the initial stages of the process, for example, ammonia in the manufacture of soda.

The chemical industry widely employs circulating water, water vapour, or cooling solutions to act as heat transfer agents. This is especially interesting when processes are carried out at high temperatures and pressures, and when they involve considerable power consumption.

4.3 Energy Flow Diagrams

Chemical reactions that evolve heat serve as heat sources. Let us imagine an exothermic reaction

$$A + B \rightleftarrows R + Q, \quad \text{e.g.} \quad N_2 + 3H_2 \rightleftarrows 2NH_3 + Q$$

To ensure a high reaction rate, high temperature is required, e.g. 500 °C in the manufacture of ammonia. It is possible to reach this temperature without the external supply of heat to the reactor, if preheated reactants are introduced into the reactor. What can be used as a heat-transfer agent? Hot reaction products may be used to heat the reactive gases. In this case, as in others, the process is comprised of conventional stages; preparation of raw materials, chemical transformations, and separation of products. At the preparation stage, the raw material is heated with products withdrawn from the reactor. Figure 38 shows such a process: the raw material is introduced for preparation into a heat exchanger (recuperator) from which the heated raw material is directed to the chemical transformation stage which occurs with heat evolution. The reaction products give off heat in the heat exchanger and are directed for separation purposes. Thus, the reaction proceeds at high temperature without an external heat supply. Such processes are called **autothermal.**

The reaction heat can be employed not only for heating purposes, but also in the production of steam in waste-heat boilers. The energy of steam can be utilized. For example,

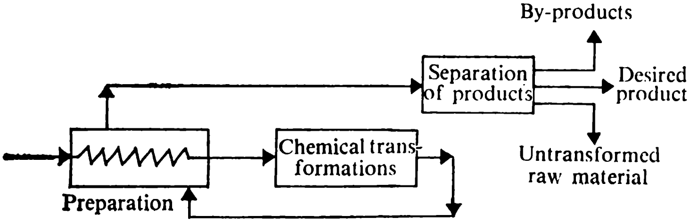


Fig. 38. Diagram of autothermal chemical transformation

the above reaction of ammonia synthesis occurs with reduced volume. Hence, in view of the Le Chatelier principle, this reaction should be carried out at high pressures. In this case, the heat of the reactive gases is recuperated not only to heat the products being fed, but also to produce steam. Such a diagram is called **energy technological** and is depicted in Fig. 39.

The preparation stage is comprised of two steps: compression and heating of gases. The compressed and heated gases are fed into the chemical transformation stage, after which they pass through a waste-heat boiler and a heat exchanger. Water is transformed into steam in the waste-heat boiler. The steam passes to the blades of the turbine located on the same shaft with the turbocompressor which compresses the reaction mixture fed for synthesis. After the waste-heat boiler, the reaction products pass through the heat exchanger, give off their heat to the compressed gases, and are directed for separation. This pattern of the diagram does not only allow a significant improvement in energy efficiency but, in a number of cases, additional power required for production is obtained. Energy technological diagrams have, at the present time, been used in industry, more particularly in the manufacture of ammonia, sulphuric acid, and other products. They have proved to be highly effective and are employed industrially on an ever increasing scale.

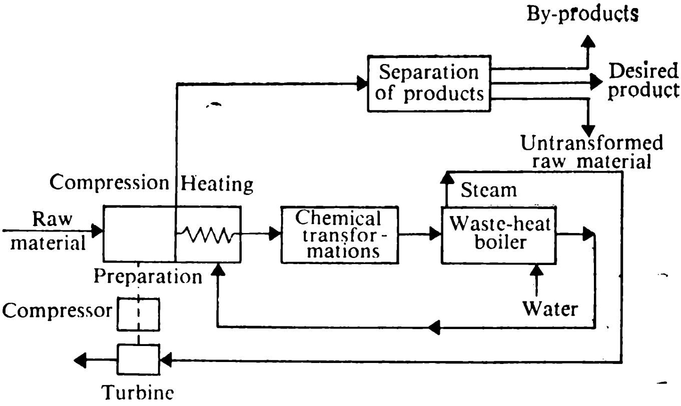


Fig. 39. Energy flow diagram

As has been indicated, the flow diagram is comprised of a number of apparatus through which the materials being processed pass. These are batch or continuously operating apparatus; they may be connected in parallel or in series.

Flows of the reacting phases may have different directions in heterogeneous processes.

4.4 Batch and Continuous Processes

Technological processes at all stages of chemical production are subdivided into batch and continuous processes by the way the starting materials are introduced into apparatus and the products removed.

Batch processes are those in which a certain amount of the initial substances is charged into an apparatus, processed for a given period of time, and when the processing is completed the apparatus is discharged. All three operations are then repeated: the raw materials are charged, then processed, and the products are discharged.

The apparatus does not operate (it is idle) when the initial substances are charged and the products are discharged, i.e. the apparatus operation time is used irrationally. Besides, intervals in apparatus operation are frequently accompanied by high irrational losses of heat or other types of energy. In batch processes it is difficult to obtain products of similar quality; these processes are difficult to mechanize or automate.

But it is sometimes advantageous to carry out batch processes at low apparatus capacity. Under such conditions, batch processes show better economic parameters as compared with continuous processes.

Continuous processes are those in which the following operations are accomplished simultaneously and continuously: the raw materials are introduced into the apparatus and processed, and the products are removed. When continuous processes are employed, there is no irrational waste of time in stopping the apparatus for charging the raw material, and discharging the products. Some processes proceed continuously for days, months, and sometimes even years. Therefore, as compared with batch processes, continuous processes are, in most cases, economically more advantageous and highly efficient. They make it possible to obtain a high yield and uniform product quality. They are easier to mechanize or automate, and they ensure that process conditions are continuous and constant.

The dominant position of continuous processes in the modern chemical industry can be attributed to these advantages.

4.5 The Direction of Flows

Continuous heterogeneous processes are subdivided into cocurrent-flow and counterflow processes, depending on the way the interacting phases are transferred.

In **cocurrent-flow processes** (Fig. 40*a*) the interacting phases move in one direction. Thus, both phases that are admitted into the apparatus possess a high concentration of reactants. The concentration of the reactants is however reduced at the apparatus outlet. Therefore, a high process rate is obtained at the apparatus inlet. But, as the flows pass through the apparatus, the rate sharply decreases and becomes insignificant at the apparatus outlet. The average conversion rate when the reactants are fed in a cocurrent flow is relatively low.

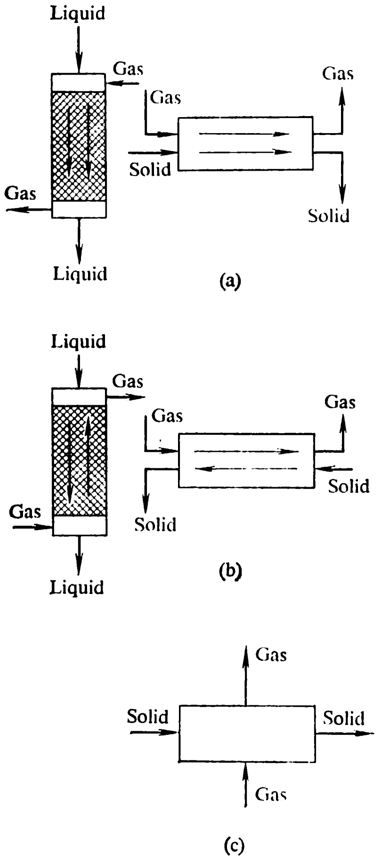


Fig. 40. Diagram showing the direction of streams

(*a*) cocurrent flow, (*b*) counterflow, (*c*) cross flow

When **counterflow** is employed (Fig. 40*b*), at the apparatus inlet and outlet, the fresh reactant in one phase is reacted with the spent reactant in the other phase. This results in the driving force of the process to be approximately the same at the apparatus inlet and outlet, and there is no sharp change in the process rate, as in the case of the cocurrent flow. The average rate of the counterflow process is higher than that of the cocurrent-flow process. Counterflow processes maintain greater interaction of the reactants; therefore, when technological processes are designed, attempts are made to ensure the interaction of the phases in the heterogeneous system employing a counterflow principle.

Counterflow is employed to effect numerous absorption processes in various industries, when a liquid is fed into absorption towers from the top, and the gases being absorbed are moving from the bottom in the direction of the liquid.

Calcination of solid materials, as well as drying in rotary tubular kilns heated with flue gases, is accomplished mainly using the counterflow principle.

Cocurrent-flow processes are predominantly employed in those cases when, due to the specific nature of interaction of the reactants, it is impossible to employ a counterflow process, for example, when ammonium nitrate is dried with heated air. When drying of ammonium nitrate with the counterflow principle, the heated air meets the dried and heated ammonium nitrate leaving the apparatus. This brings about a partial decomposition of the ammonium nitrate and results in greater losses of the product.

The **cross flow** is mainly used for the effective utilization of energy. In particular, processes are organized in a manner so as to utilize the heat of the waste gases or the reaction products to preheat the raw material (Fig. 40*c*), for example, in the oxidation of SO_2 to SO_3 and the synthesis of ammonia (Fig. 33). Such energy recovery results in a considerable saving of energy resources and, thus, making the products being manufactured much cheaper.

Chapter 5

ENVIRONMENTAL PROTECTION

In our dynamic century, in addition to the admiration of man's success in mastering and "conquering" nature, there is a growing concern by the people of the world for the state of the environment. This concern has been a grave anxiety for the last two decades.

Concern for environmental protection has become a state policy in the Soviet Union. As early as the first years of Soviet power, V. Lenin had signed a number of important decrees on the protection and rational utilization of land, water, and forest resources, mineral resources, plant and animal world, and on the protection of historic and natural monuments.

Air is polluted with the carbon monoxide contained in automobile exhaust gases, atmospheric discharges of industrial fuels (primarily in the power industry, and also for home heating and vehicles). Other pollutants are sulphur dioxide derived from combustible fuels and also contained in gaseous waste products of the chemical industry, nitric oxides, hydrocarbons, lead, mercury, and radioactive isotopes contained in the exhaust gases at some enterprises. These substances do not remain long in the atmosphere. They fall on the Earth's surface or return with atmospheric precipitation. They are carried away by wind to other regions of the globe. It should be noted that chemical enterprises produce smaller amounts of exhausts into the atmosphere than those produced at power industry enterprises or by vehicles. However, the waste gases of the chemical industry are highly toxic. For example, sulphur dioxide contaminates all living things and destroys, by its corrosive action, metal constructions and structures located near the enterprises.

Water (running or stagnant) is the habitat of plants and animals. Water pollution imperils the existence of some water fauna. The main dangers for water are petroleum and petroleum products, industrial waste (for example, in the wood-pulp and paper, and chemical industries), phenols, domestic garbage which contains large quantities of detergents, and chemical fertilizers and pesticides that drain into rivers and lakes from the fields when agriculture is run irrationally.

Soil is contaminated with solid waste like refuse dumps and slimes of industrial and mining enterprises, dust and soot from gas exhausts, and also domestic garbage and dumping grounds.

Solid waste in part penetrates the soil not only as solid particles. It is exposed to atmospheric moisture, i.e. washed out with underground waters, and then penetrate in dissolved form basins polluting them.

Thus, various industrial wastes, irrespective of their state of aggregation, disturb the flora and fauna, and finally disturb the vital activity of man.

Therefore, environmental protection is an integral part of man's life. It is inseparably connected with the establishment of links between the organism and environment, with the investigation of the changes taking place in nature owing to industrialization. Research into these problems and finding ways to protect the environment are the concern of the science called **ecology**.

The problems of environmental protection are of paramount importance in the Soviet Union, since it is inseparably linked with improving labour conditions and recreation of the Soviet people. In connection with this fact, the maximum permissible concentration of chemicals in air, water, and soil has been, for the first time, worked out and approved by the Soviet Government.

The *maximum permissible concentration* (MPC) is the concentration of a substance which does not affect man directly or indirectly, does not reduce his working ability nor produces any adverse effect on his state of health and mind. At the present time, 160 standard documents that determine the MPC of various substances in the atmosphere, and about 500 standard documents for basins, have been approved in the Soviet Union. The MPC values are given in monographs and reference books. It should be noted that the MPC of chemicals in air and water adopted in the Soviet Union are the world's strictest values.

5.1 Basic Trends in Environmental Protection

Environmental protection may be effected basically by four means: (1) by setting up waste-free industrial complexes or individual industries, (2) by reducing or eliminating industrial effluents, (3) by reducing or eliminating pollution of the atmosphere by gaseous exhausts from combustible fuels; (4) by utilizing and rendering harmless industrial waste and exhausts at the operating enterprises.

Waste-free industrial complexes or individual industries are designed on the basis of the integral utilization of all raw material. This process can be accomplished by several means, one of the most rational ones by calculating the reaction mixture, and the so-called introduction of recycling into the flow diagram. In this case, after the reaction products are separated the unreacted raw material is returned to the process. Processes of this type are widely employed, for example, in the synthesis of ammonia from nitrogen and hydrogen and in the synthesis of methanol. As a result, the starting material is completely utilizated and no waste exists.

Industrial effluents are reduced or eliminated by creating effluent-free "dry" industries.

At the present time, recycling and the multiple use of waste are widely employed industrially for this purpose, namely returning waste waters after purification to the same process, i.e. recirculation, the use of waste waters after completion of one industrial stage to the other stage, the use of waste waters after purification for various technological processes, and other needs.

Pollution of the atmosphere with gaseous exhaust in the combustible fuels containing sulphurous and other toxic compounds *is reduced or eliminated* by purifying fuels of these compounds prior to their combustion. For example, liquid fuels are subjected to special purification from sulphur by catalytic hydrogenation. To reduce the sulphur content in solid fuels, they are beneficiated and purified to remove sulphur-containing mineral impurities.

At the present time, the problem of environmental protection is being solved by using new types of fuels whose combustion does not produce any toxic substances. Hydrogen and methanol are such fuels.

Utilization and rendering harmless industrial waste and effluents at operating enterprises is one of the widely employed methods for reducing industrial effluents. To this end, enterprises process waste into valuable products. The manufacture of phosphoric acid by decomposition of natural phosphates with sulphuric acid is an example. In this case, so-called phosphogypsum ($CaSO_4 \cdot 2H_2O$) is formed which is a waste product. At the present time, methods for processing phosphogypsum to form cement, an essential building material, are being developed.

However, it should be noted that waste products are not processed in all chemical industries. For example, the manufacture of calcined soda produces large quantities of the-so-called "still waste" containing calcium chlorides, sodium and ammonium salts. The problem of utilizing this industrial waste has not, up to the present time, been solved on a wide scale. To eliminate solid and liquid waste products, they are, in a number of cases, buried by the operating enterprises. In this case, soil may not only be polluted, but toxic substances may penetrate underground waters. Biological cleaning of waste products is also of interest.

The above-mentioned means for environmental protection indicate that the creation of waste-free industries which employ a closed cycle are proving to be highly rational and effective. Waste-free industries are solving the social problem of the elimination of effluents.

5.2 Methods for Purifying Gas Exhausts

Gas exhausts may contain, firstly, suspended particles of solid substances, such as dusts, and liquids (mist). Such systems are called **aerosols**, and, secondly, gaseous and vapourous substances.

Purifying of gases from aerosols is basically accomplished mechanically or electrostatically.

Mechanical purifying from aerosols includes dry and wet methods. *Dry methods* include gravity, inertial and centrifugal dust collection, and filtration.

Gravity deposition is based on the gravity deposition of particles contained in a gas. In this case, the gas flows in a gas conduit or in a dust chamber at a low rate and the direction of flow remains unchanged. As the gas flows, the suspended particles become separated. When gravity deposition occurs, the degree of gas purification is 40-50%. This method may therefore be recommended only for rough gas purification.

Inertial deposition is based on the tendency of suspended particles to retain their initial direction of motion when the gas flow changes its direction. To this end, the contaminated gas passes through louvers (slots). The gas flow changes its direction and the suspended particles are separated from this flow. This method assures a degree of gas purification between 20 and 70%; it may be employed for rough gas cleaning. The disadvantage of the method is that the slots become worn out and clogged up.

Centrifugal purification methods are based on the action of centrifugal forces which arise when a gas flow rotates, Cyclones are used for this purpose. The gas flow is admitted into the cyclone tangentially, i.e. tangent to the surface of the circumference of the cyclone cross section, and moves in a spiral manner inside the apparatus. The suspended particles fall out of the gas flow. The degree of gas purification depends on particle size and may amount to about 90%. Cyclones are employed for rough and medium gas cleaning.

Filtration is based on passing a gas through a filter media, such as fabrics. Filters are subdivided into fabric filters which employ cotton, wool, chemical fibres, and glass fibre for filtration purposes, and those employing granular materials, such as ceramics, cermet, and plastic materials.

Filtration assures fine gas purification and makes it possible, once an appropriate filter medium is chosen, to purify aggressive gases at elevated temperatures.

The disadvantage of filtration is that there is high hydraulic pressure and the filter medium becomes clogged up; this causes disturbance in the technological conditions.

Wet purification of a gas from aerosols comprises washing gases with water in an apparatus having a developed contact area between the gas being cleaned and the wash liquid. To do this, packed towers are used. The degree of gas purification in these apparatus is 80%. It should be noted that when separation of solid particles occurs, the packing rapidly becomes clogged with dust. The main disadvantage of the method of wet gas purification from aerosols is that large amounts of liquid waste products containing solid particles (slimes) or liquid particles are formed when separated from the gases. Thus, if these waste products are not used anywhere, the wet gas purification method cannot be recommended.

Electrostatic gas purification from aerosols is based on the fact that when gas passes through an electric field of high voltage (25 to 100 kV), the suspended particles contained in the gas become charged and deposit on the electrodes, thus causing removal of particles from the gas flow. Apparatus employed for this purpose are called **electric precipitators.** Electric precipitators assure a degree of gas purification of 99.9%. They can operate within a wide range of temperature (from minus 20 °C to 500 °C), and offer a low hydraulic resistance, therefore they are widely employed for fine gas purification. At the same time, it should be noted that the use of electric precipitators involves the consumption of considerable electric power. •

Purification of gas from vaporous and gaseous impurities, such as carbon monoxide and dioxide (CO, CO_2), sulphur dioxide (SO_2), nitrogen monoxide and dioxide (NO, NO_2), and other various organic compounds is accomplished in three ways: by absorption, i.e. dissolution of gaseous impurities in liquids, adsorption, i.e. deposition of impurities on the surface of solid materials, and **catalytic transformations** which produce harmless compounds from the harmful impurities contained in gases.

Thus, there are three methods of gas purification, namely absorptive, adsorptive, and catalytic purification.

Absorptive purification is employed both for removing harmful impurities from gases so as to intensify the technological processes in which they are used, and for sanitary cleaning, i.e. to protect the environment.

Absorptive purification is effective if the liquid absorbent possesses great absorbing power (capacity), i.e. if it possesses a high dissolving power for the component being recovered from the gas mixture. In this case, dissolution of the gas may occur without chemical interaction between the gas and the liquid: **physical** gas absorption takes place. Recovery of carbon dioxide with water from gas mixtures is an example. In a number of cases, the gaseous component being absorbed may be removed from the gas mixture by chemical interaction with some substance dissolved in a liquid. For example, aqueous solutions are used to remove carbon dioxide from gas mixtures. Such a process is called **chemisorption**. Absorbing solutions used in industrial conditions should possess not only a high absorbing power. They should also dissolve readily and at a high rate the substance being recovered from the gas, rather than absorb the valuable components from this substance. Hence, it is essential that a solvent should be **selective**. The equilibrium vapour pressure of the solvent should be minimum so that the vapours may not contaminate the gas mixture being purified. The solvent should be cheap and should not cause corrosion of the apparatus.

It is exceedingly important that the absorber can be regenerated, i.e. the gases dissolved in this absorber may be desorbed and the absorber may be reused. Thus, a continuous waste-free cyclic gas purification process is accomplished.

The absorbing solution can be regenerated either by heating or by lowering the pressure, thus causing liberation of the absorbed gases from the liquid.

Since absorption gas purification is essentially a heterogeneous process, in order to accelerate it, the contact surface of the interacting phases should be enlarged. This can be accomplished by fitting an apparatus with packed or tray-type columns. Figure 41 shows diagramatically an absorption-desorption plant.

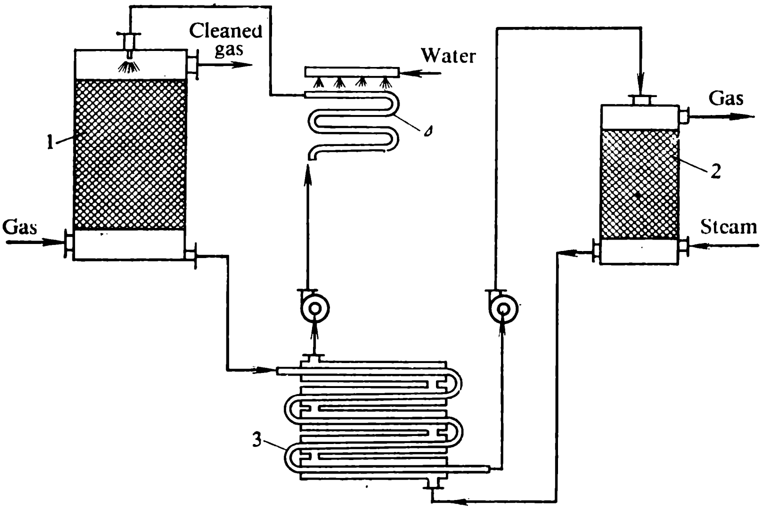


Fig. 41. Diagram of absorption-desorption plant
1—absorber; 2—desorber; 3—heat exchanger; 4—cooler

Absorption methods are advantageous in that they allow continuous processes to be run and they are economical making it possible to recover a large amount of noxious impurities from gases. At the same time, they do not assure a high degree of recovery of harmful impurities.

Adsorptive purification is employed for the separation of gas mixtures, desiccation of gases, and for sanitary gas purification, i.e. for environmental protection.

When adsorptive purification •takes place, solid highly porous materials (**adsorbents**) are used to recover harmful impurities from gases. Adsorbents have a highly developed surface where the impurities removed can be deposited.

Activated carbon, silica gel, alumogel, and zeolites (molecular sieves) are used as adsorbents.

As the adsorbents make contact with the gas being purified, the surface is filled up and the adsorbent capacity decreases. In order to regenerate the adsorbent, the adsorbed substance should be removed (desorbed) from the surface. To this end, the adsorbent is heated by passing steam, air or some inert gas, such as nitrogen. The activity of the adsorbent is restored and it may be used for gas purification.

Thus, a batch process will occur with altenating adsorption-desorption stages.

To have a continuous process, it is essential to have a plant which consists of several adsorbers: in some adsorbers adsorption will occur, and in the other adsorbers, desorption will occur with these stages adjusted for various operating conditions (Fig. 42).

Adsorption purification is advantageous in that it permits excellent gas purification and purification of gases with a low impurity content. Adsorption processes are disadvantageous in that they are batch processes, and more complex plants are needed for continuous regeneration.

Catalytic purification is used for removing impurities, such as sulphur-containing and organic compounds, oxides of carbon and nitrogen, and other substances, from gases.

Catalytic oxidation, reduction, and hydrogenation of toxic impurities are carried out on catalysts.

For example, sulphur-containing compounds are oxidized to sulphur dioxide followed by oxidation to sulphur trioxide from which sulphuric acid is derived. Nitric oxide is reduced with hydrogen to elementary nitrogen, and carbon monoxide is hydrogenated to form methane.

Catalytic purification methods are now being widely used, since they make it possible to remove 99.9% of toxic impurities from gases. Catalytic purification is not complex, simple in operation and small in size.

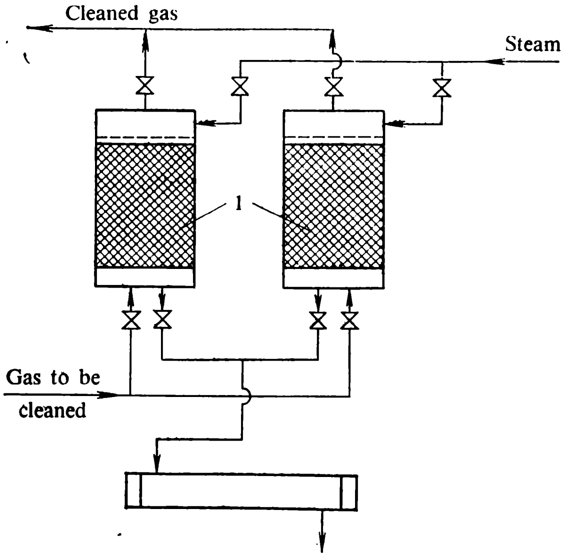


Fig. 42. Diagram of absorption plant
1—absorber; 2—condenser

Catalytic cleaning is disadvantageous in that catalysts must be regenerated. In connection with this fact highly effective catalysts with a long service life should be developed for some processes.

5.3 Sewage Treatment Methods

The basic sources of water contamination are as follows:

Chemical	Biological	Physical
Acid	Bacteria	Heat
Alkali	Viruses	Colour
Salt	Other pathogenic organisms	Odour
Pesticide	Algae	Radioactivity
Detergent	Feces	Suspended solid substances
Phenol or other organic compounds	Lignins	Sand
Some cations		Slime

They may be present in sewage, industrial sewage included, and have a toxic effect on the biosphere. Industrial sewage may be classified according to different principles: by origin, i.e. by industries, sewage produced by petrochemical, by-product core, and other industries; by nature of the technological processes, sewage resulting from distillation, absorption, mixing, etc.; by phase-dispersion, sewage containing solid particles of various size, suspended particles of liquids (emulsions), etc.; by composition, sewage containing phenols, cyanides, organic acids, etc.

Sewage treatment methods may be subdivided into four groups: mechanical, physicochemical, chemical, and biological.

Mechanical cleaning is based on particles falling by gravity. It separates impurities by settling, clearing, and filtration. To this end, settling tanks, grids, filters, and cyclones are used. Mechanical cleaning is employed to separate large-size particles.

Physicochemical purification is based on the difference between the physicochemical properties of water and the impurities it contains. This treatment includes the processes of flotation, coagulation and flocculation, solvent extraction, distillation and rectification, and adsorption. These methods are employed for removing finely divided, colloidal, and also dissolved substances.

Chemical purification is employed to neutralize acids and alkalis, and to precipitate impurities. This method involves formation of compounds that are precipitated and special equipment is required to separate them. In addition, unfortunately, these precipitates cannot always be used and, therefore, may contaminate the soil.

Biological purification is a widely used method. It is based on the oxidation of organic and inorganic compounds by some microorganisms. Oxidation produces harmless substances, such as water, carbon dioxide, nitrate and sulphate ions, and also the so-called "activated sludge". The composition of activated sludge includes various bacteria.

There are two methods of biological purification of sewage: the **aerobic** method, when atmospheric oxygen is continuously fed, and the **anaerobic** method, when no oxygen is fed. The aerobic method has found the widest application.

Certain conditions are needed for **aerobic** purification. The temperature should not exceed 40 °C, the pH, 5.5-8.5, and the oxygen content in water should be at least 1 mg per dm^3. Vigorous agitation is essential to maintain the activated sludge in a suspended state. For aerobic purification, ammonium sulphate and nitrate, carbamide, and superphosphate are generally added to sewage. The presence of these substances promotes the normal activity of microorganisms.

Aerobic purification is used on agricultural irrigation fields, in biological ponds, biological filters, and aerotanks.

Agricultural irrigation fields are sewage purification works based on purifying properties of soil, air and the sun, and the activity of plants.

Biological ponds are essentially a cascade of shallow artificial basins with natural or artificial aeration (treatment with air). The water being purified passes through these basins at a very slow rate. When artificial aeration is not employed, the residence time for sewage in ponds exceeds 60 days. When artificial aeration is employed, this time is reduced to 1-3 days.

Biological filters are reactors filled with a packing (Fig. 43) on whose surface a biofilm composed of microorganisms is formed. Slimes, crushed stone, expanded clay aggregate, coke, claydite, and plastic blocks are used as packing. Dissolved and suspended organic compounds in the water are adsorbed and then oxidized on the biofilm. Biofilters are used as one of the stages of purification in combination with biological ponds and aerotanks.

Aerotanks are noted for their high capacity. They are essentially reinforced concrete reservoirs into which the water to be purified and air are continuously fed. Microorganisms develop in the water, and activated sludge is formed. To feed air and enlarge its contact surface with water, the aerotanks are provided with bubblers, nozzles, and diffusers from a porous plastic material.

Aerotanks may be manufactured in the form of successively connected passages (corridors) through which water is moving continuously (Fig. 44) and into which air is fed. The total length of the corridors is 20 to 100 m, and the operating depth is 3.5 m.

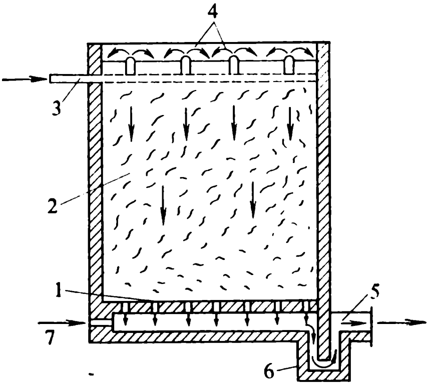


Fig. 43. Diagram of forced aeration biofilter

1—bearing grid; *2*—charging of filter; *3*—pipe for feeding waste water; *4*—water distribution devices; *5*—chute for removing purified water; *6*—hydraulic seal; *7*—pipes for supplying air

Aerotank mixers are reactors that agitate the reaction mixtures. Agitation may be done by air (Fig. 45) or a stirrer.

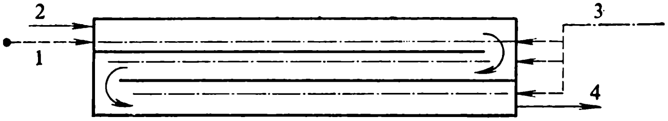


Fig. 44. Diagram of corridor aerotank

1—activated sludge; *2*—sewage; *3*—air; *4*—removal of excess sludge

The aerotank mixers operate continuously and their capacity is several hundreds of cubic metres of water per day. They assure a high degree of water treatment.

When aerotanks operate continuously, activated sludge is continuously formed. Therefore, to maintain the desired technological conditions, excess sludge is removed. The sludge is dehumidified and dried. The dry residues are either

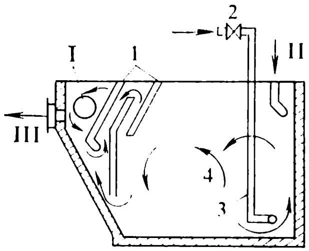


Fig. 45. Diagram of a pneumatic aeration aerotank mixer

1—degassing section; *2*—pipeline for feeding compressed air; *3*—pneumatic aerator; *4*—aeration zone; *I*—removal of purified water; *II*—waste water to be purified; *III*—removal of excess sludge

burned or used as fertilizer. In the latter case, the activated sludge is subjected to special sanitary-hygienic treatment. The decontaminated activated sludge may also be used as a concentrate feed for agricultural animals.

The biological method for sewage treatment has found wide application. The method assures complete oxidation and decontamination of sewage, it involves the use of simple apparatus, and low operating costs.

The method is disadvantageous in that the oxidation rate is low, which is due to large volumes of purification works.

Chapter 6

MANUFACTURE OF SULPHURIC ACID

6.1 Properties and Uses of Sulphuric Acid

Sulphuric acid is one of the most important products of the chemical industry. Anhydrous sulphuric acid, or monohydrate, is an oily liquid that is heavier than water. The density of sulphuric acid (mass of 1 ml at 0 °C) is equal to 1.84 g/cm^3, while the density of water is 1 g/cm^3 in the same conditions.

Sulphuric acid shows high chemical activity, i.e. it readily enters into chemical reactions. It reacts vigorously with metals, displaces other acids from their salts, and combines avidly with water. Wood, other plants, and also living tissue are rapidly decomposed by sulphuric acid and become black. Those handling sulphuric acid should be especially careful.

The high chemical activity of sulphuric acid makes it possible to manufacture acid derivatives or other substances by using this acid.

Sulphuric acid is virtually used in all chemical industries. It serves as one of the major chemical products that determine the development of the chemical industry. It is not without reason that it is called "the bread of chemistry". The chemical industry employs sulphuric acid for the manufacture of fertilizers, such as superphosphate, ammonium sulphate, and ammophos. About half of the acid produced in the Soviet Union is used for the manufacture of fertilizers.

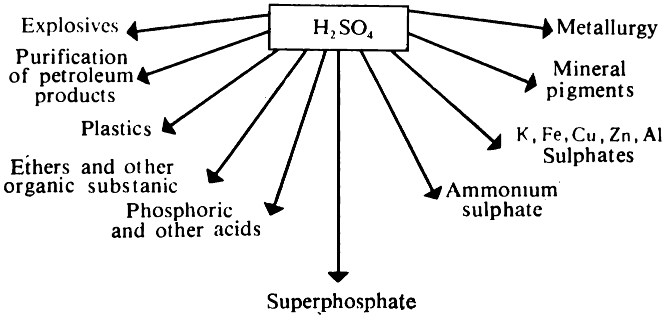

H_2SO_4
Explosives
Purification of petroleum products
Plastics
Ethers and other organic substanic
Phosphoric and other acids
Superphosphate
Ammonium sulphate
K, Fe, Cu, Zn, Al Sulphates
Mineral pigments
Metallurgy

Diagram 8. Application of sulphuric acid

Sulphuric acid is employed in the manufacture of dyes, plastics, chemical fibres, and pharmaceuticals. Considerable amounts of sulphuric acid are consumed in the production of petroleum products, such as liquid fuels and lubricating oils.

Sulphuric acid is consumed not only in the chemical industry. Recovery of metals from ores in the iron and steel industry, pickling of metals at engineering plants, treatment of fibres and fabrics with dilute sulphuric acid solutions, prior to dyeing at textile factories and manufacture of starch, syrup, and alcohol at the food industry enterprises are an incomplete list of the applications of sulphuric acid. Great importance is attached to sulphuric acid for the needs of the defence industry: it is employed in the manufacture of explosives and gunpowder (Diagram 8).

The great need for sulphuric acid has determined the scale of its manufacture. The world's annual production of sulphuric acid is about 100 million tons. The USSR is second in the world in sulphuric acid production.

Sulphuric acid used in industry is called an **industrial** acid; these are aqueous sulphuric acid solutions. The content (concentration) of sulphuric acid in these solutions may be different, for example, *tower acid* contains 75 to 78% H_2SO_4 and 22 to 25% H_2O. *Contact acid* is manufactured in large quantities, and is more concentrated and purer than a tower acid, containing 92.5% H_2SO_4 and 7.5% H_2O. Solutions of sulphur trioxide (SO_3) in sulphuric acid called *oleum* have been widely used. Oleum contains 18 to 20% SO_3, the balance is H_2SO_4. Characteristics of the grades of sulphuric acid manufactured under industrial conditions are reported in Table 2.

TABLE 2. **Grades of Sulphuric Acid**

Acid	Content, % by mass	
	H_2SO_4	SO_3
Contact acid:		
industrial	92.5	—
industrial, improved	92.5-94	—
Oleum	81.5	18.5
Tower acid	75.0	—

6.2 Raw Materials for the Manufacture of Sulphuric Acid

The process for producing sulphuric acid involves two reactions:

$$2SO_2 + O_2 = 2SO_3 \tag{6.1}$$

$$SO_3 + H_2O = H_2SO_4 \tag{6.2}$$

Equation (6.1) describes the oxidation of sulphur dioxide to sulphur trioxide. Equation (6.2) shows the reaction between sulphur trioxide and water to form sulphuric acid. It follows from Eqs. (6.1) and (6.2) that oxygen obtained from air, water, and sulphur dioxide are necessary for the production of sulphuric acid.

Hence, air is the first raw material in the manufacture of sulphuric acid, water the second, and sulphur dioxide the third. Where does sulphur dioxide come from? Sulphur or sulphur-containing materials are used as raw materials in the production of sulphur dioxide and, hence, sulphuric acid.

Sulphur is a yellow solid substance having a melting point of 113 °C and a boiling point of 444.6 °C. Sulphur occurs naturally in "sulphur ores", in which sulphur is blended with other substances. When sulphur ore is heated, sulphur flows out in molten state. One of the methods for recovering sulphur from sulphur ores is based on this principle.

Sulphur pyrite is a yellowish grey stone with bright disseminations, and contains the pyrite mineral (FeS_2). The sulphur content in pyrite varies from 35 to 50%, and the iron content, from 30 to 43%. The balance includes impurities, such as compounds of copper, zinc, lead, arsenic, and selenium. Sulphur pyrite mined at pyrite deposits is brought to chemical plants as lumps of various sizes. This pyrite is called run-of-the-mine pyrite.

In addition, sulphur pyrite may be derived from the copper ores used to produce copper and containing FeS_2. Processing copper ores at special concentrating mills produces a product containing much copper (copper concentrate) and waste (flotation tailings) rich in sulphur pyrite. The copper concentrate is sent to copper smelteries, and the waste products (flotation tailings, which are the major raw material in the manufacture of sulphuric acid) are sent to chemical plants. Thus, copper ores are completely used.

Gases from steelmaking furnaces, in which ores of copper, zinc, and other nonferrous metals, are processed, contain sulphur dioxide. These gases flowing out of the furnaces pollute the atmosphere, cause damage to vegetation, and have an adverse effect on people.

Sulphur can be made from these gases using these reactions:

$$2H_2S + O_2 = S_2 + 2H_2O \qquad (6.3)$$

$$2CS_2 + 2SO_2 = 3S_2 + 2CO_2 \qquad (6.4)$$

$$4CO + 2SO_2 = S_2 + 4CO_2 \qquad (6.5)$$

The use of the nonferrous waste gases is of great importance to the national economy, since it simultaneously solves two problems, i.e. how to produce sulphuric acid without consumption of sulphur pyrite or sulphur, and how to render the atmosphere harmless.

Hydrogen sulphide is separated from the gases of coal and petroleum processes. Hydrogen sulphide is oxidized with atmospheric oxygen to sulphur dioxide:

$$2H_2S + 3O_2 = 2SO_2 + 2H_2O \qquad (6.6)$$

or to elementary sulphur:

$$2H_2S + O_2 = 2S + 2H_2O \qquad (6.7)$$

Here, the resulting SO_2 or sulphur is used to manufacture sulphuric acid.

6.3 Manufacture of Sulphur Dioxide

Processing of sulphur. To produce sulphur dioxide, sulphur is burned in air. In this case, the following reaction occurs:

$$S + O_2 = SO_2 \qquad (6.8)$$

Sulphur combustion is done in furnaces which are simple to design and produce sulphur dioxide uncontaminated with harmful impurities.

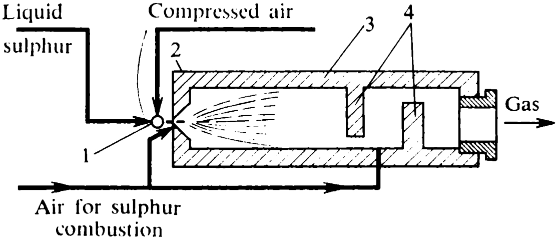


Fig. 46. Sulphur combustion furnace

1—burner; *2*—horizontal steel cylinder; *3*—refractory brick lining; *4*—partitions

The furnace for sulphur combustion (Fig. 46) is essentially a steel cylinder *2* lined with refractory brick *3*. The molten sulphur is fed by air into the furnace through burner *1*.

To better agitate the products, the furnace interior is provided with partitions *4*. Sulphur is ignited at high temperatures in the furnace to form a jet of the burning sulphur. Sulphur combustion occurs throughout the furnace and is completed in the chambers formed by partitions *4*. An additional amount of air is supplied into the chambers. The hot furnace gas which contains sulphur dioxide is withdrawn from these chambers.

Processing of sulphur pyrite. This process is defined by the following reaction:

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2 + 3324\ \text{kJ} \qquad (6.9)$$

As is apparent from Eq. (6.9) when FeS_2 is reacted with atmospheric oxygen, a considerable amount of heat is liberated with the result that the furnace temperature, at which the process is carried out, rises to 700 to 800 °C. The pyrite roasting products are a roast or furnace gas which contains about 8 to 10% SO_2 and about 10 or 11% oxygen. The balance is nitrogen, admitted into the furnace together with air, and pyrite cinder, which is a red-brown product containing basically iron oxide.

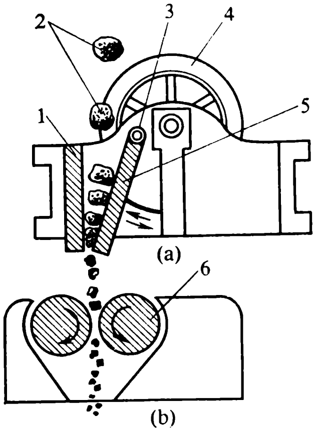


Fig. 47. Diagram of pyrite grinding process

(*a*) in jaw crushers; (*b*) in roll crushers; *1*—fixed jaw; *2*—pyrite; *3*—steel shaft; *4*—fly wheel; *5*—movable jaw; *6*—roll

Pyrite roasting occurs intensively at high temperatures since the reaction rate is enhanced. Pyrite roasting is a heterogeneous process and, therefore, in order to intensify the process, it is necessary to have the largest surface of contact possible between pyrite particles and the air. This can be achieved by grinding pyrite and stirring it in the air stream during the roasting process.

Grinding of sulphur pyrite, if it is brought to the factory as large-size lumps, is first processed in jaw crushers (Fig. 47*a*). The crusher has two plates or "jaws", jaw *1* is fixed and jaw *5* is movable. Pyrite is fed into the space between the plates. The movable jaw suspended to steel shaft *3* is periodically closed on the fixed plate crushing the pyrite between them. After the jaw crusher, the pyrite lumps are still relatively large, they are then fed to be finally ground by a roll crusher (Fig. 47*b*) with two steel cylinders (rolls) which rotate towards each other.

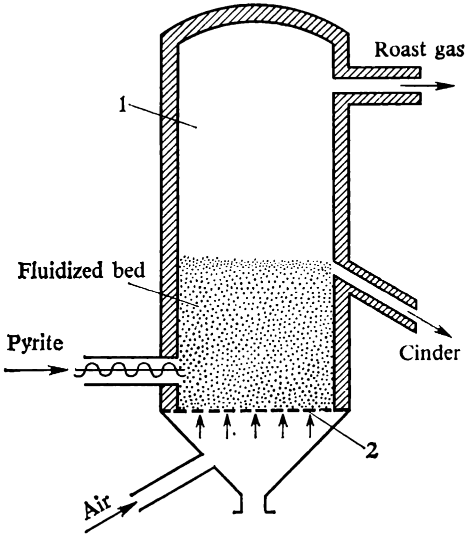


Fig. 48. Fluidized bed furnace
1—chamber; *2*—grid

Pyrite roasting is done in furnaces of different construction at a temperature of about 800 °C. Fluidized bed furnaces have found the widest application.

The fluidized bed furnace (Fig. 48) is essentially a vertical, hollow chamber *1* at the bottom of which is grid *2* (it resembles a fire grate). Finely crushed pyrite is continuously fed to the grid, and air is blown in under the grid. The air passes through the grid holes at a high rate, lifts and stirs the pyrite on the grid. The pyrite layer externally resembles a boiling liquid (hence the name, a "fluidized" bed furnace). The temperature inside the furnace is about 800 °C. The gas is withdrawn from the top of the furnace, and the cinder, through overflow pipe. 100 t of pyrite can be roasted daily in fluidized bed furnaces.

The gas leaving the roasting furnaces carries away fine cinder particles. The roast gas should be cleaned from dust so as not to contaminate the acid, which will be produced, or clog up the equipment.

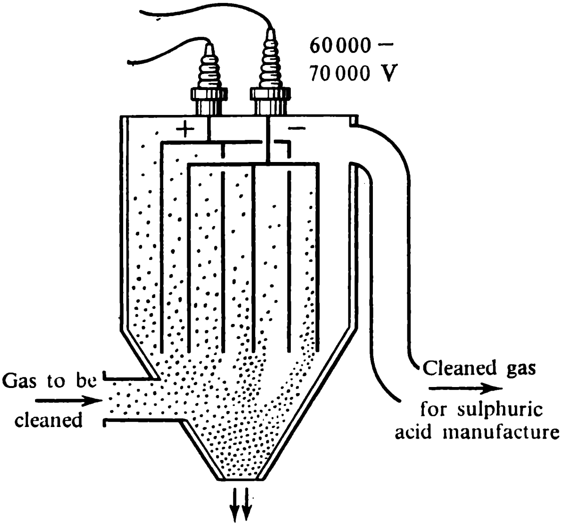


Fig. 49. Electric precipitator

Cleaning of the Roast Gas from Dust. This process is most successfully carried out in electric precipitators. Their operation is shown in Fig. 49. The electric precipitator is supplied with direct current at a high voltage of 60 000 to 70 000 V. Dust particles become negatively charged in the d.c. field of this voltage, are moved to the positively charged electrode, then become discharged, and fall. Cleaned from dust, the roast gas contains about 9% SO_2, 9 or 10% O_2, and about 80% N_2.

Cinder. The cinder resulting from pyrite roasting contains up to 50% of Fe. About 0.6 t of cinder is produced from 1 t of sulphuric acid. Thus, the annual amount of cinder amounts to millions of tons, which can be used in cast iron making. However, the cinder removed from roasting furnaces is unsuitable to use directly in blast furnace processes, for it is very small in size and contains nonferrous metals at levels that exceed those permissible for a blast furnace. Therefore, prior to feeding the cinder to blast furnace smelting, it is preliminarily treated. The cinder may also be used for manufacturing cement and for making mineral dyes.

6.4 Conversion of Sulphur Dioxide into Sulphuric Acid

Sulphuric acid is produced from sulphur dioxide by reacting sulphur dioxide with the oxygen contained in the roast gas (see Eq. 6.1). This process produces sulphur trioxide (SO_3) which is then absorbed by water to form sulphuric acid (see Eq. 6.2). The first reaction occurs exceedingly slowly in ordinary conditions.

Depending on the method of oxidation of SO_2 to SO_3, sulphuric acid is produced by two processes.

The Contact Process. This process for producing sulphuric acid is described by the two reactions just mentioned:

$$2SO_2 + O_2 = 2SO_3 \tag{6.1}$$

$$SO_3 + H_2O = H_2SO_4 \tag{6.2}$$

In ordinary conditions, sulphur dioxide is not oxidized to sulphur trioxide, since this reaction proceeds at a very slow rate. To accelerate the reaction, a vanadium catalyst containing vanadium pentoxide, V_2O_5, is used. Catalysts are sometimes called "contacts". Therefore, this method is called the contact method for producing sulphuric acid.

The catalyst operates for a long period and needs not be replaced with a fresh one provided the roast gas is cleaned not only from dust but also from other harmful impurities, like As_2O_3, SeO_2, and water vapour that gets on the catalyst during pyrite roasting.

The roast gas cleaning (Fig. 50) begins with the removal of dust in an electric precipitator. The gas is then admitted into gas wash towers *1* and *2* which are sprayed with dilute sulphuric acid. The acid cools the gas and dissolves arsenic and selenium compounds, thus partially removing them from the gas. The gas is washed with dilute sulphuric acid to form misty sulphuric acid containing As_2O_3. If the mist particles

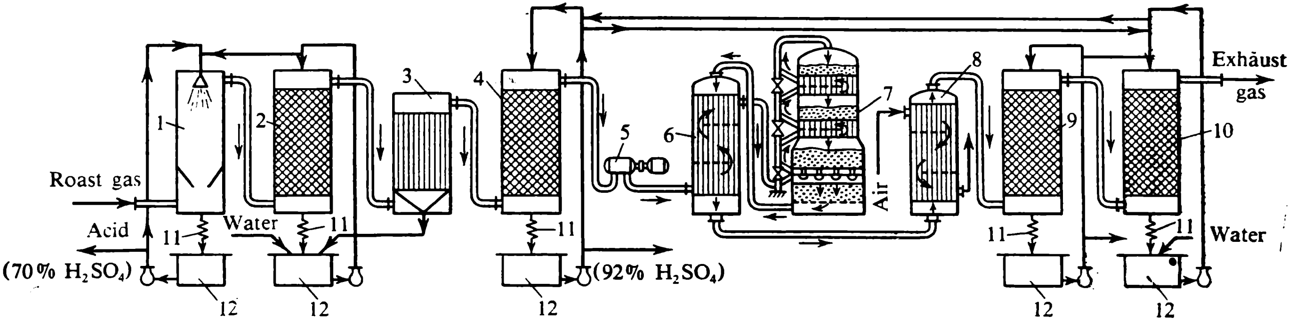


Fig. 50. Flow diagram of manufacturing sulphuric acid by a contact process

1—holow scrubber wash tower; *2*—packed scrubber tower; *3*—"wet" electric precipitator; *4*—drying tower; *5*—turbocompressor; *6*—heat exchanger; *7*—catalytic reactor; *8*—tubular cooler; *9*—oleum absorber; *10*—monohydrate absorber; *11*—acid coolers; *12*—acid collectors

happen to fall on the catalyst, they "poison" the catalyst rendering it inactive. The mist particles are therefore removed by the so-called "wet" electric precipitator *3*. Its operation is similar to that of an electric precipitator for the deposition of dust, i.e. the mist particles are ionized in a high voltage field and are then discharged across the electrode. After passing the "wet" electric precipitator, the gas is cleaned from water vapours in the packed tower *4* sprayed with concentrated sulphuric acid. This tower is called a drying tower. After passing the tower, the gas is transferred to catalytic apparatus *7* through heat exchanger *6* for the oxidation of SO_2 to SO_3.

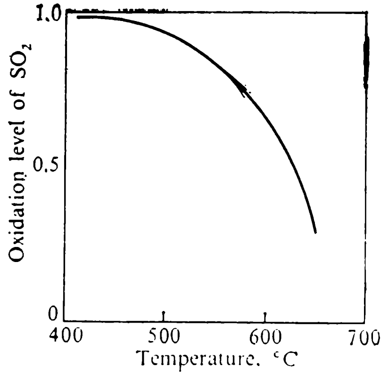


Fig. 51. The optimal temperature condition for SO_2 oxidation (the course of the process is indicated by the arrow)

The oxidation of SO_2 to SO_3 is a reversible reaction, which liberates heat:

$$2SO_2 + O_2 \rightleftarrows 2SO_3 + 190\ \text{kJ} \qquad (6.10)$$

As is known, in this case to shift the reaction equilibrium from the left to the right, it is expedient to carry out the process at low temperatures. However, the reaction will proceed at a very slow rate at low temperatures, and the degree of conversion of SO_2 to SO_3 will prove to be very low. In view of this fact, a temperature is chosen so that the reaction rate will be high and the degree of conversion will also be quite high. This is called the optimal temperature for the reaction (6.10).

Since reaction (6.10) is reversible, the process is begun at a high temperature, to assure a high rate, then the temperature is gradually lowered to shift the equilibrium towards formation of sulphur trioxide (Fig. 51). This is possible due to the special design of the catalytic apparatus.

The catalytic apparatus (Fig. 52) has two shelves *2* onto which catalyst *1* is poured. Tubular heat exchangers *3* are located between the shelves holding the catalysts. The gas is admitted into the apparatus from the bottom and then passes through the intertube space of the heat exchangers where the gas is heated to 450 °C by the heat exchange with the gases that have passed through the catalyst. At 450 °C the gas is admitted into the first bed of the catalytic mass. There, SO_3 (6.10) is formed with heat evolution, and the gas temperature rises.

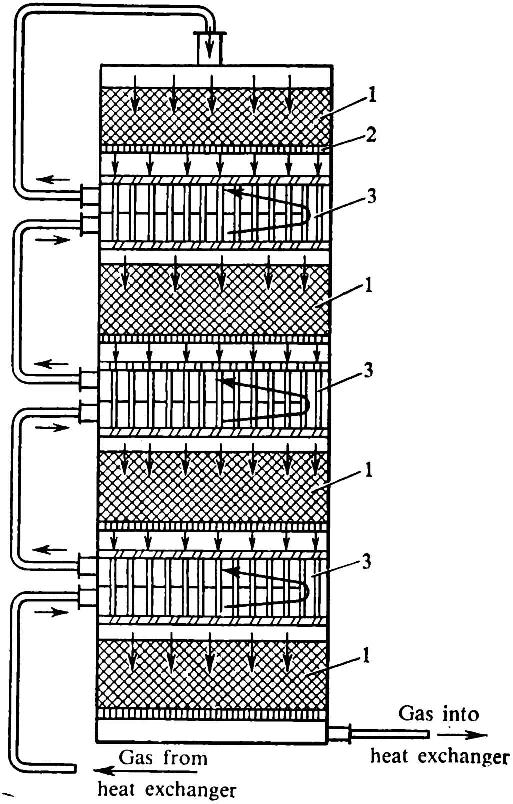
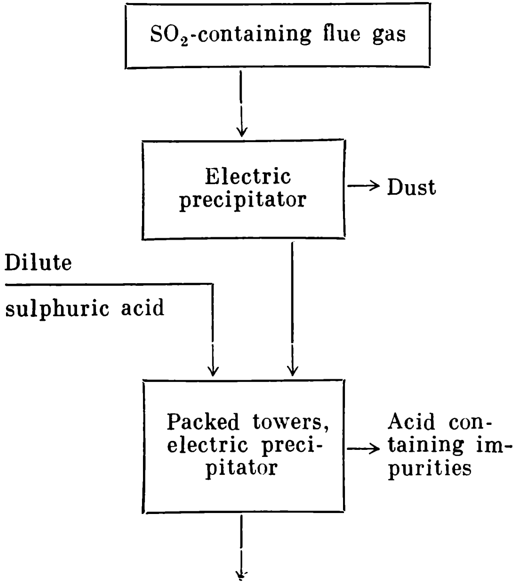


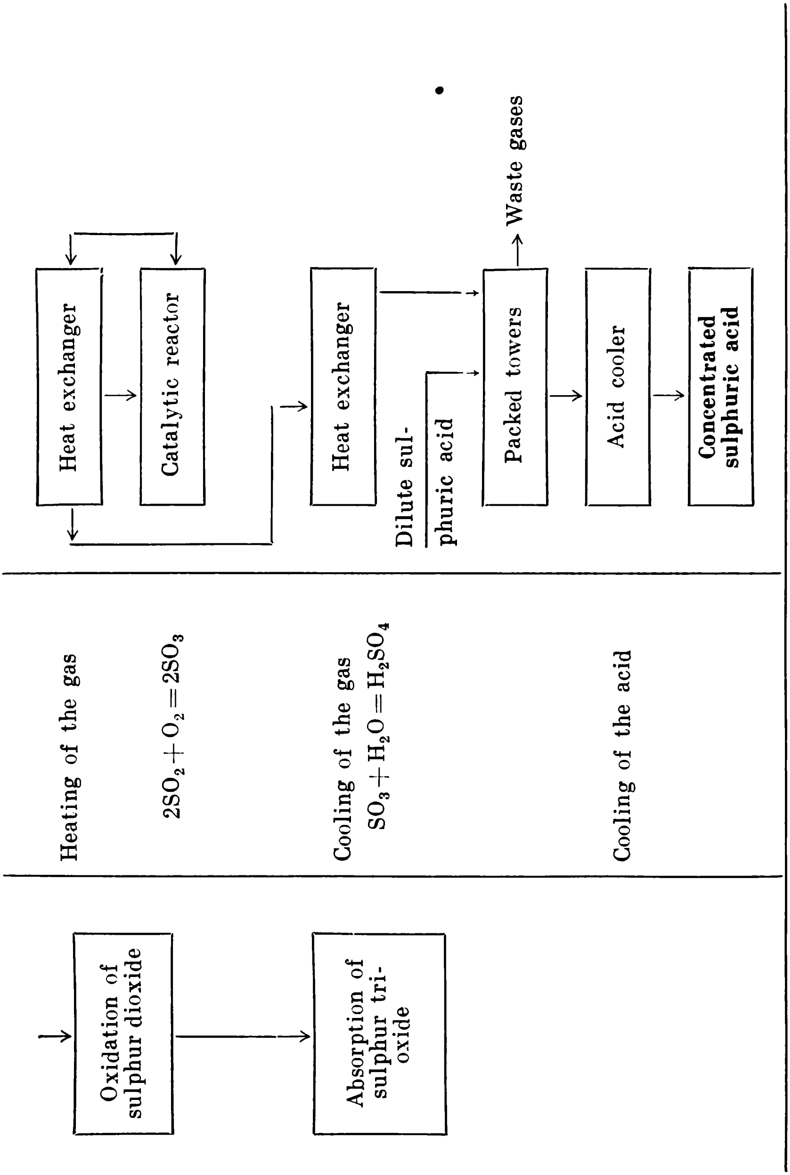
Fig. 52. Catalytic reactor

1—catalyst; *2*—shelf; *3*—heat exchangers

TABLE 3. **Manufacture of Sulphuric Acid by the Contact Method**

Process	Operations	Apparatus employed
Preparation of the gas	Removal of dust from the gas	
	Cooling of the gas and removal of harmful impurities	

SO_2-containing flue gas
Electric precipitator
Dust
Dilute sulphuric acid
Packed towers, electric precipitator
Acid containing impurities


Oxidation of sulphur dioxide
Absorption of sulphur trioxide
Heating of the gas
$2SO_2 + O_2 = 2SO_3$
Cooling of the gas
$SO_3 + H_2O = H_2SO_4$
Cooling of the acid
Heat exchanger
Catalytic reactor
Heat exchanger
Dilute sulphuric acid
Packed towers
Waste gases
Acid cooler
Concentrated sulphuric acid

The gas leaving the first bed of catalyst mass *1* is admitted into the tubes of upper heat exchanger *3* where this gas is cooled with the gas in the intertube space. This gas is intended to make contact with the former gas. The gas is then allowed to pass into the second bed of catalyst mass *1*, where reaction (6.10) occurs. The gas becomes heated again and then gives off its heat to the second heat exchanger, and so on. Thus, the desired temperature is established to oxidize sulphur dioxide.

A high-power catalytic apparatus that has a daily capacity of 1000 to 1200 t of H_2SO_4 is being built now.

To produce sulphuric acid, it is necessary to absorb sulphur trioxide with water (see Eq. (6.2)), or with sulphuric acid. To this end, the hot gas leaving the catalytic apparatus, having a temperature of about 450 °C, is cooled in tubular cooler *8* (Fig. 50), and then admitted into absorbers *9* and *10* sprayed with sulphuric acid. Either a concentrated (contact) acid or an oleum resulting from the dissolution of sulphur trioxide in sulphuric acid flows from the tower.

The contact method for the production of sulphuric acid is shown diagrammatically in Table 3.

Methods for the production of sulphuric acid may be compared after examining the characteristics of the nitrous and contact methods for sulphuric acid production. The methods are presented in Table 4.

It is apparent from Table 4 that the contact process produces a more concentrated and purer acid, which is more ex-

TABLE 4. **Comparison of Nitrous and Contact Methods for the Production of Sulphuric Acid**

Characteristic	Nitrous method	Contact method
Acid concentration, % by mass	75	92.5-94
		Oleum, 18.5-20 SO_3
Impurities	Arsenic compounds, nitric oxides	—
Power consumption, kW·h/t	30-40	60-100
Cost of 1 t, roubles	21.10	29.60

pensive than that produced by the nitrous process. The contact acid is used to manufacture fibres, plastics, dyes, ethanol, etc. The tower acid is mostly used when an acid of high concentration is not required, for example, in the manufacture of fertilizers.

6.5 Concentration of Sulphuric Acid

Most industries consuming sulphuric acid require concentrated acid. Transporting a weak acid, such as tower acid, over long distances is unprofitable, since such an acid contains as little as 75% of the valuable substance, 25% being water. Such an acid is generally used at the enterprise that manufactures it, or the acid is concentrated.

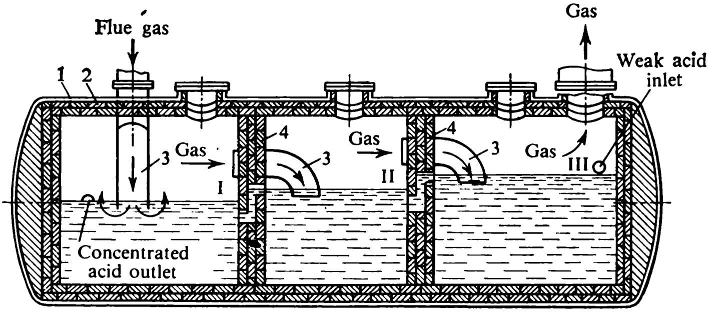


Fig. 53. Drum-type concentrator

1—horizontal drum; *2*—lining (andesite); *3*—pipe; *4*—partitions

Concentration is done by removing the water contained in the acid by heating a weak sulphuric acid, which evaporates water, concentrating the acid. Hot flue gases resulting from the combustion of coal, fuel oil, and natural gas are used as the heat source. The apparatus for concentrating the acids are called **concentrators**.

The drum-type concentrator with the widest industrial application (Fig. 53) is horizontal steel drum *1* lined with acid-proof material *2* (andesite). The interior is divided into three chambers by partitions *4*. The flue gases are admitted into chamber *I* through pipe *3*, and from chamber *I* pass successively through chambers *II* and *III*. The weak acid is admitted into chamber *III* and moves in counterflow to the flue gases through chambers *II* and *I*. As the pipes along which the gases pass are immersed into the acid, they are bubbled through the acid. The gases give off their heat to the acid, which becomes concentrated up to 92 or 93 per cent

6.6 Materials Used to Manufacture the Apparatus for Sulphuric Acid Production

When choosing materials to manufacture apparatus used to produce sulphuric acid, the following should be taken into account: the resistance of these materials to corrosion by sulphuric acid and the resulting gaseous products, and also their stability at high temperatures. Almost all apparatus used to produce sulphuric acid are manufactured from steel and iron, and are lined mostly with acid-proof materials (ceramic and natural acid-proof materials, like andesite, stone casting, and acid-proof concrete), organic acid-proof coatings, plastics (faolite, vinyl chloride plastic, polyisobutylene, etc.).

6.7 Storage and Transportation of Sulphuric Acid

Sulphuric acid is stored only in steel tanks located in the building or under a shelter which shields the top of the tanks from atmospheric precipitation. Sulphuric acid is carried long distances in tank cars that have a weight carrying capacity of up to 60 tons. When small lots of sulphuric acid are transported they are carried in tank trucks, containers, steel carboys having a capacity of up to 0.2-1 ton or glass carboys having a capacity of 30 to 45 litres which are placed into baskets or bracings. The space between the carboy and the bracing is filled with straw or wood shavings.

6.8 Perspectives in the Development of Sulphuric Acid Production

A great number of new sulphuric acid plants are now under construction in the Soviet Union. The scope of sulphuric acid production, as envisaged by the plan, is such that capacities of the former apparatus cannot cope with this task.

Therefore, there arose a problem of working out new highly efficient flow diagrams and designs for apparatus with high capacity and intensity (for example, catalytic reactors having a daily capacity of 1200 tons of acid or more).

The maximizing of the mechanization and automation of sulphuric acid production is a serious task. Sulphuric acid plants should be fully automated. Catalyst masses for the sulphuric acid industry should be improved. Operating temperatures of masses should be lowered and their strength improved. Using gases with a high SO_2 content and carrying out processes at elevated pressures are of interest; this allows intensifying the processes.

It is of no small importance to manufacture airtight sulphuric acid apparatus and to eliminate noxious gas exhausts from the plant. Waste (exhaust) gases should be cleaned of SO_2, nitric oxides and sulphuric acid mist as much as possible. Removing SO_2 from the flue gases of thermal stations which use coal with a high sulphur concentration, and the use of SO_2 in sulphuric acid manufacture are a major problem for the national economy. It is essential not only for improving the sanitary and hygienic working and living conditions in the industrial regions, but also for eliminating the fast corrosion of metals at the enterprises located in the areas adjoining thermal stations. It is also important to use cinders at sulphuric acid plants as raw material in the production of some metals, including precious metals.

REVIEW QUESTIONS

1. Name some applications for sulphuric acid.
2. What raw material is sulphuric acid derived from?
3. Write the equation of FeS_2 oxidation reaction.
4. Draw the diagram of a furnace for roasting pyrite.
5. How is the roast gas cleaned from dust?
6. What reactions occur when the tower method is employed to manufacture sulphuric acid?
7. According to the diagram presented in the book, describe the nitrous process for manufacturing sulphuric acid.
8. What is the essence of the process used for cleaning the roast gas when the contact process is employed to manufacture sulphuric acid?

9. Enumerate the factors that determine the degree of conversion of SO_2 to SO_3.
10. Draw the diagram of a catalytic reactor.

Chapter 7

MANUFACTURE OF AMMONIA

7.1 Nitrogen Compounds and Their Importance for the National Economy

The Concept of Free and Fixed Nitrogen. Nitrogen, as translated from Greek, means "not maintaining life". It is also called a "dead gas". It came to be known so because it reacts neither with metals nor with non-metals under ordinary conditions. In addition, this name is rather conventional because nitrogen is incorporated in proteins, forms highly important nutrients, and thus plays a very significant role in the living nature of our planet and in the life of people. From this point of view, it would be more correct to call nitrogen "the source of life". However, nitrogen is incorporated in explosives and, in this case, it does mean "not maintaining life".

Gaseous (atmospheric), or free, nitrogen present in the air by itself is of limited practical importance. It is used in an admixture with argon for filling electric bulbs; free nitrogen is employed for creating inert medium for carrying out chemical reactions at laboratories and plants.

The organic and inorganic compounds that incorporate fixed nitrogen are of immense importance.

Nitrogen is constantly circulating in nature. In the first stage, atmospheric nitrogen is bound into compounds, i.e. atmospheric nitrogen is fixed. This can be done in two ways. The first is combining free atmospheric nitrogen, during atmospheric electricity discharges, i.e. during lightning discharges, with atmospheric oxygen. The resulting nitric oxides are combined with atmospheric precipitation to form nitric and nitrous acids which penetrate the soil where they are transformed into nitrates and nitrites. The second way is fixing atmospheric nitrogen due to activity of special fixing bacteria in the soil. Plants do not generally assimilate or absorb nitrogen from the air. Some bean plants, such as lucerne, lupine, and other plants have tubercles filled with bacteria at their roots. These bacteria or microorganisms penetrate plants from the soil; they fix and collect atmospheric nitrogen. In addition to tuber bacteria atmospheric nitrogen is fixed with bacteria freely living in soil, i.e. nitrobacteria.

Nitrogen compounds present in the soil in a solution form are absorbed by the plant roots and then, due to a large number of complex biochemical processes, form nitrogen-containing organic compounds, such as proteins. Since plants serve as animal fodder and foodstuffs for man, their proteins become the source for animal proteins. As dead animals and plants decay, the proteins decompose, the final decomposition product being ammonia and free nitrogen. Most of the ammonia nitrogen in the soil is transformed into nitrates by nitrifying bacteria and atmospheric oxygen. The nitrates are dissolved in water, absorbed by plant roots, and then transformed into proteins, and so on.

In addition, proteins are decomposed in the soil by denitrifying bacteria to form free nitrogen. The free nitrogen is then fixed, and so on.

Uses of Fixed Nitrogen. The content of nitrogen compounds that can be assimilated by plants in the soil is very low, and therefore atmospheric nitrogen is the basic source for nitrogen nutrition in plants. As outlined above, there are two methods in nature for fixing atmospheric nitrogen and replenishing nitrogen resources in the soil, i.e. electric discharge and nitrogen fixing bacteria. However, this is not sufficient. Therefore, there arose a problem of providing plants with nitrogen nutriment to increase the crop yield by introducing nitrogen-containing compounds, i.e. nitrogen fertilizers, into soil.

The powerful development of synthetic materials (polymers) manufacture is inseparably linked with need for nitrogen-containing products. The plastic material industry requires nitrogen compounds to manufacture amino plastics, transparent acrylic plastic, celluloid, and other materials. Fixed nitrogen is used to manufacture synthetic fibres, such as capron, nylon, some synthetic rubbers, and paint coatings. Significant amounts of nitrogen compounds are used to manufacture aniline dyes and other chemical products.

In addition to biological and industrial applications, fixed nitrogen is of great importance for the defence industry, since it is incorporated in explosives and powders.

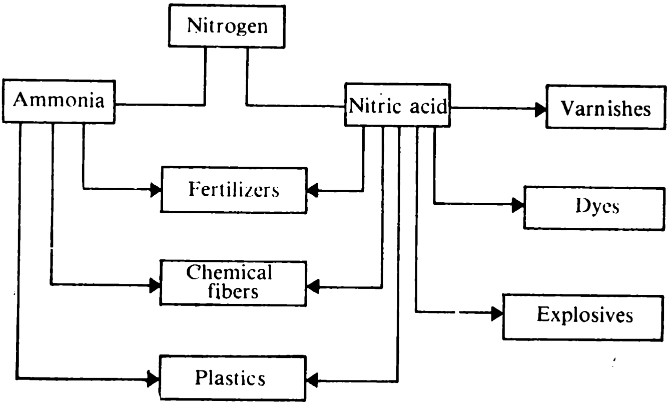


Diagram 9. Nitrogen application

Ammonia and nitric acid are the simplest and most important starting products in the manufacture of nitrogen compounds. The high reactivity of ammonia and nitric acid made it possible to use them to manufacture nitrogen-containing products, such as nitrogen fertilizers, plastics, chemical fibres, and aniline dyes (Diagram 9).

7.2 Methods for Fixing Atmospheric Nitrogen

Natural Sources of Fixed Nitrogen. Manure, guano (mineralized bird manure), and sodium nitrate, $NaNO_3$, are the oldest sources of industrial fixed nitrogen. Sodium nitrate deposits are found in some countries, including the Soviet Union. But sodium nitrate deposits are important industrially only in Chile (South America), its reserves are estimated to be about 8 billion tons. Hence, sodium nitrate is called "Chilean". Potassium nitrate, KNO_3, deposits are found in India.

A natural source of fixed nitrogen is also a solid fuel, i.e. fossil coals which are processed to produce ammonia.

Despite the development of coal processing, the amount of ammonia produced together with the Chilean and potassium nitrates are insufficient to meet the needs of agriculture and industry for nitrogen compounds. Science has turned to ambient air for the source of nitrogen. Air is indeed an inexhaustible source of nitrogen; air contains millions of times more nitrogen than required to run successfully agriculture and develop industries.

D. Mendeleev was the first to advance the scientific problem of fixing atmospheric nitrogen. In 1869 he wrote: "One of the problems of applied chemistry is to seek for a technically advantageous process for deriving compounds comprised of assimilable nitrogen from atmospheric nitrogen. The future of agriculture will depend a great deal on the discovery of such a process".

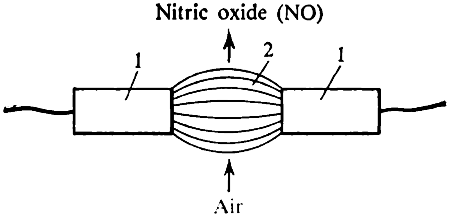


Fig. 54. Diagram of an arc method for fixing nitrogen

1—electrode; *2*—arc

Methods for Nitrogen Fixing. By the beginning of the 20th century, developing methods for fixing atmospheric nitrogen had been taken on as the major scientific and engineering problem. The solution of this problem was made difficult due to the fact that nitrogen is inert, i.e. it does not readily enter into chemical reactions. Some method had to be found, which would make atmospheric nitrogen combine with other elements. In 1902-1903 the arc method for nitrogen fixing was the first such process, nitrogen and atmospheric oxygen were reacted at temperatures of 2000 °C to 2500 °C. The process occurring during lightning discharges was reproduced on an industrial scale. The electric furnace (Fig. 54) has electrodes *1* along which a high voltage current is flowing. The electrodes are located at some distance apart, and an electric arc *2* is formed between them. The arc temperature is 2000 °C to 2500 °C. Air is blown through the arc, and nitrogen and atmospheric oxygen react in the arc flame at high temperatures:

$$N_2 + O_2 = 2NO \tag{7.1}$$

to form a colourless gas, i.e. nitric oxide. Free atmospheric nitrogen is fixed with oxygen to form nitric oxide which is then processed into nitric acid.

The substantial disadvantage of this process is the exceedingly high power consumption, i.e. 60 000 to 70 000 kW·h per ton of fixed nitrogen. This is why after some more economical methods for fixing atmospheric nitrogen had been devised, the arc method rapidly lost its significance.

The cyanamide method for nitrogen fixing was introduced in 1905-1910. In this process atmospheric nitrogen reacts with calcium carbide in an electric furnace at 1000 to 1100 °C according to this reaction:

$$CaC_2 + N_2 = CaCN_2 + C \tag{7.2}$$

The resulting calcium cyanamide can be used as a nitrogen fertilizer or processed into ammonia and nitric acid.

Power consumption is also rather high in this method; 10 000 kW·h per ton of fixed nitrogen. In view of this fact, a more economical method for fixing atmospheric nitrogen was sought.

The synthesis of ammonia from its basic elements (nitrogen and hydrogen) was developed in Germany in 1913. It proved to be considerably more advantageous than the arc and cyanamide methods, and rapidly replaced them becoming the predominant method for fixing atmospheric nitrogen in the world.

At the present time, about 94 per cent of the world's fixed nitrogen is manufactured by this method.

Formation of ammonia from the elements occurs according to the reaction:

$$3H_2 + N_2 = 2NH_3 \tag{7.3}$$

Ammonia is a colourless gas with a very sharp and typical odour. When cooled, ammonia becomes liquefied, readily dissolves in water, and then easily enters into reactions to give ammonium salts and other compounds. An aqueous solution of ammonia is called ammonia water or spirits of hartshorn. Inhaling small amounts of ammonia causes irritation of the respiratory tract, large amounts cause dyspnoea, fits of cough, dizziness, and convulsions. As can be seen from Eq. (7.3), the raw materials for this process are hydrogen and nitrogen, the latter being derived from atmospheric air.

7.3 Manufacture of Nitrogen from Air

Air is a complex mixture of gases. Given below is the composition of air (the gas composition is indicated in per cent by volume):

Nitrogen	78.09	Helium	0.00046
Oxygen	20.95	Neon	0.0016
Argon	0.93	Krypton	0.00011
Carbon dioxide	0.03	Xenon	0.000008

It is evident from these data that the bulk of air is composed of nitrogen and oxygen (99.04%).

Nitrogen is derived from air by separating it from oxygen and other gases. This process is based on the difference in the boiling points of nitrogen and oxygen; nitrogen boils at atmospheric pressure and a temperature of minus 196 °C, and oxygen, at a temperature of minus 183 °C, i.e. nitrogen has a lower boiling point than oxygen.

In ordinary conditions air is a colourless gas. But if air is "deeply cooled", i.e. cooled to a very low temperature, minus 192 °C, it becomes a colourless liquid. If liquid air is heated, nitrogen will be evaporated, and oxygen will remain as a liquid. This process is called free air rectification. Thus, nitrogen is derived from air, for the synthesis of ammonia.

The resulting oxygen is employed in large amounts in the steel-and-iron, chemical, and other industries.

7.4 Manufacture of Hydrogen

Hydrogen is rarely found free in nature. It is manufactured by several methods: water electrolysis, conversion of carbon monoxide, methane conversion, and separation of a coke-oven gas. The choice of the method is determined by the economical aspects of the process, i.e. by the cost of the hydrogen produced, since the preparation of a nitrogen-hydrogen mixture is the most costly stage in the manufacture of ammonia.

The electrolysis of water is done by immersing electrodes into water and passing direct current through it. Water decomposes into hydrogen and oxygen, and hydrogen is deposited on the cathode (the negatively charged electrode), and oxygen, on the anode (the positively charged electrode). This process makes it possible to manufacture highly pure hydrogen and oxygen. However, this process has a high electric power consumption rate and therefore it can be employed if cheap electric power is available. This process is rarely employed to manufacture hydrogen in the synthesis of ammonia.

Carbon monoxide conversion is done by passing carbon monoxide and steam through a catalyst at a temperature of 250 to 525 °C:

$$CO + H_2O \rightleftharpoons CO_2 + H_2 + 20\ \text{kJ} \qquad (7.4)$$

This produces hydrogen and carbon dioxide. The gas is then cleaned of carbon dioxide, thus producing the hydrogen used in ammonia synthesis.

Carbon monoxide employed in the conversion process is contained in producer gases resulting from the processing of solid fuels, mostly coals. Hence, steam and coal are the raw materials in the production of hydrogen by this method.

Methane Conversion. As outlined above, natural gases are a more economical fuel than coals. Therefore, use of these gases to produce hydrogen and process gases in ammonia and methanol synthesis is of interest. Natural gases contain up to 98 per cent of methane. Turning these gases into hydrogen is done by deriving hydrogen from methane using steam and oxygen. This process which came to be called methane conversion is described by the following reactions:

$$CH_4 + H_2O \rightleftarrows CO + 3H_2 - 203\ \text{kJ} \tag{7.5}$$

$$CH_4 + \frac{1}{2}O_2 \rightleftarrows CO + 2H_2 + 36\ \text{kJ} \tag{7.6}$$

The resulting carbon monoxide is then converted into hydrogen according to reaction (7.4). As the reaction (7.5) is reversible and occurs with heat absorption, the equilibrium is shifted by carrying out the reaction at a high temperature of about 1400 °C (high temperature conversion). The

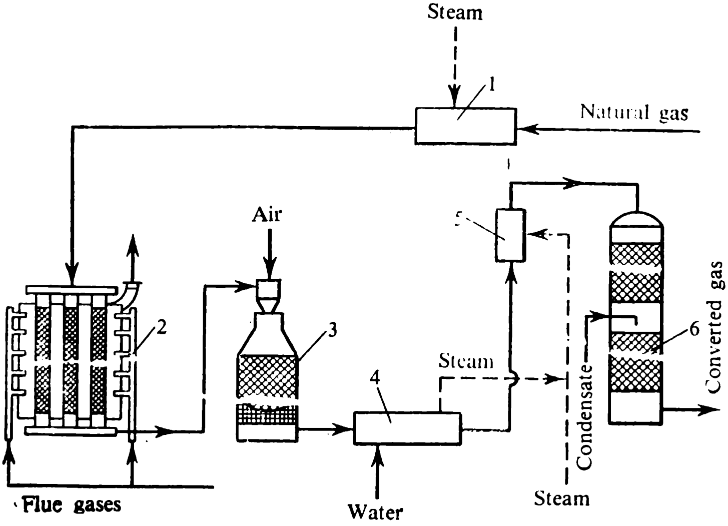


Fig. 55. Diagram of catalytic conversion of methane

1—gas-vapour mixer; *2*—tubular catalytic reactor (tubular methane converter); *3*—capacity-type catalytic reactor (shaft-type methane converter); *4*—waste-heat boiler; *5*—gas-vapour mixer; *6*—shaft-type catalytic reactor (carbon monoxide converter)

process is carried out in the presence of a catalyst at a temperature of 800 to 900 °C (catalytic conversion). The catalyst is nickel applied on alumina or magnesium oxide. The nickel catalyst is sensitive to impurities of sulphur compounds in the gas.

The hot flue gases resulting from the combustion of natural gases may serve as a heat source. Here, when catalytic conversion occurs, tubular catalytic reactor *2* (Fig. 55) is used, A nickel catalyst is present in the reactor tubes, and the hot flue gases are passing along the intertube space.

The heat required to convert CH_4 with steam may be produced according to reaction (7.6). In this case, a mixture of natural gas and air or oxygen is used.

Figure 55 shows the diagram for processing natural gases. Natural gas preliminarily cleaned from sulphur-containing compounds is mixed with steam in gas-vapour mixer *1*. The resulting gas-vapour mixture (the vapour/gas ratio is 2.5 : 1) is directed into tubular catalytic reactor *2*, which is the first stage for the conversion of methane. About 70 per cent of the methane is converted in the converter at a temperature of 700 °C. The gas is directed from the tubular catalytic reactor into capacity-type catalytic reactor *3* as the second stage. Air required for carrying out the exothermic reaction (7.6) is introduced into this converter. The temperature is maintained in the converter at about 850 °C. Air is introduced into the second stage converter in such amounts so that, after the oxygen contained in free air reacts with methane, the nitrogen to hydrogen ratio is 1:3 (such a ratio is essential for ammonia synthesis).

From the second stage converter, the hot gas is admitted into waste-heat boiler *4* where the heat is used to convert water into steam. From the waste-heat boiler the gas is directed into gas-vapour mixer *5* into which steam is fed, which is essential for carbon monoxide conversion according to reaction (7.4), and into carbon monoxide converter *6*. Condensate is introduced into converter *6* to reduce the temperature when the reversible exothermic reaction (7.4) occurs. Then, the gas is cooled and fed for cleaning purposes.

The definite economic efficiency of using natural gases to manufacture ammonia is the reason why they are used at most nitrogen fertilizer plants. In addition to natural gases, other methane-containing gases, e. g. casing-head, coke-oven, and oil-refinery gases, are used in the synthesis of ammonia.

Separation of Coke-Oven Gases. The process for separating coke-oven gases to produce hydrogen has found extensive application. Coke-oven gas results from heating coal without air at a temperature of 800 to 1050 °C. Composition of the coke-oven gas and the boiling point of its constituents at atmospheric pressure are presented in Table 5.

TABLE 5. **Composition of the Coke-Oven Gas and the Boiling Points of Constituents**

Constituent	Content, %	Boiling point, °C
H_2	55-59	—252.6
N_2	5-6	—195.7
CO	5-7	—191.7
CO_2	1-3	—79.9
CH_4	23-28	—161
Higher hydrocarbons	2-3	from —40 to —103
O_2	0.3-0.8	—183

It is clear from the table that all coke gas constituents, except for hydrogen, have a boiling point higher than —252.6 °C. Thus, if the coke gas is cooled to a temperature higher than minus 252.6 °C, for example, —200 °C, all the constituents will liquidize, and only hydrogen will remain gaseous. This is the principle on which the production of hydrogen from coke-oven gas is based.

7.5 Gas Purification

To synthesize ammonia, a nitrogen-hydrogen mixture must be purified as fully as possible from the oxygen- and sulphur-containing compounds which are catalytic poisons. After the methane conversion, in addition to hydrogen and nitrogen, the gas contains about 30 per cent CO_2, 0.3 to 4 per cent CO, 0.5 per cent CH_4, 0.5 per cent Ar, and traces of H_2S.

The industrial gas purification methods are many. They are generally subdivided into three main groups: (1) gas purification by liquid absorbers (absorbents); (2) by solid adsorbers (adsorbents) or by catalysts (dry method); (3) purification by freezing, i.e. converting impurities into liquid or solid state.

Purification of industrial gas from carbon dioxide is generally done by liquid absorbers. The absorbents used include water, monoethanolamine solutions, and hot potash solutions.

Water purification of gas is based on the fact that carbon dioxide is readily dissolved in water. At a pressure of 25 to 35 MPa, the converted gas is admitted into the bottom of the packed tower sprayed with water. The washed gas is withdrawn from the top of the tower. The water flowing out of the tower is fed to the turbine where water pressure decreases, and the absorbed carbon dioxide is derived from water. The water is again fed for spraying absorption towers.

Purification with ethanolamine is effected with aqueous solutions of mono- or diethanolamines: $(CH_2CH_2OH)NH_2$ and $(CH_2CH_2OH)_2NH$. Let us designate CH_2CH_2OH as R, and monoethanolamine as RNH_2. The main reactions of the gas purification are:

purifying from CO_2:

$$2RNH_2 + H_2O + CO_2 \rightleftarrows (RHNH_2)_2CO_3 \tag{7.7}$$

purifying from H_2S:

$$2RH_2 + H_2S \rightleftarrows (RHNH_2)_2S \tag{7.8}$$

Amine carbonate and sulphide resulting from the absorption of CO_2 and H_2S relatively readily decompose when the solution is regenerated. The regeneration is done by heating the solution to 120 °C to liberate CO_2 and H_2S. After regeneration, monoethanolamine solution is again fed for spraying the absorbers.

In some cases, carbon monoxide is removed from the gas and washed at a pressure of up to 300 kgf/cm^2 and at a temperature from 0 °C to 30 °C with an ammoniacal solution of copper acetate:

$$[Cu(NH_3)_2]CH_3COO + CO + NH_3 \rightleftarrows [Cu(NH_3)_3CO]CH_3COO \tag{7.9}$$

The solution is regenerated by heating and reducing the pressure.

After purifying the nitrogen-hydrogen mixture with liquid absorbers, it contains small amounts of CO and CO_2 (up to 1 per cent) which can contaminate catalyst.

Methanation or hydrogenation removes the residuals of CO and CO_2 from the gas. The gas is fed to a nickel catalyst over which the following reactions occur at 200 to 400 °C:

$$CO + 3H_2 = CH_4 + H_2O \qquad (7.10)$$

$$CO_2 + 4H_2 = CH_4 + 2H_2O \qquad (7.11)$$

The resulting methane does not reduce catalyst activity in the synthesis of ammonia.

7.6 Ammonia Synthesis

The Theoretical Fundamentals of Ammonia Synthesis. Ammonia synthesis is one of the more highly perfected chemical technological processes. As previously indicated, the synthesis is described by the reaction of nitrogen with hydrogen:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + 92\ \text{kJ} \qquad (7.12)$$

This reaction is reversible. It occurs with volume reduction (two volumes of ammonia are derived from four volumes of the nitrogen-hydrogen mixture), and heat is evolved. Hence, using the Le Chatelier principle, the equilibrium of reaction (7.12) can be shifted towards ammonia formation, by using high pressure and low temperature with a high concentration of nitrogen and hydrogen in the gas used in the synthesis (Table 6).

TABLE 6. **The Equilibrium Ammonia Content in the Synthesis Gas**

Temperature, °C	NH_3 content (%) at different pressures (kgf/cm^2)		
	100	300	1000
200	—	89.94	98.29
300	—	70.96	92.55
400	25.12	47.00	79.82
500	10.61	26.44	31.43
600	4.52	13.77	12.83

It is clear from Table 6 that higher pressure and lower temperature increase the ammonia concentration in the synthesis gas. In view of this fact, all industrial plants for the synthesis of ammonia operate at pressures of hundreds of atmospheres. As to the temperature, the reaction rate is so insignificant at low temperatures that the reaction practically does not occur. Therefore, to make the reaction proceed at an industrially advantageous rate, it should begin at high temperatures which may then be lowered to attain a sufficiently high degree of conversion of the nitrogen-hydrogen mixture (Fig. 56).

But this is not sufficient to carry out the process at a high rate. As in some other cases (for example, in the oxidation of sulphur dioxide), the reaction can be accelerated by a catalyst, such as iron in the form of spongy pieces or tablets with alumina and potassium additives to make catalyst activity high and stable.

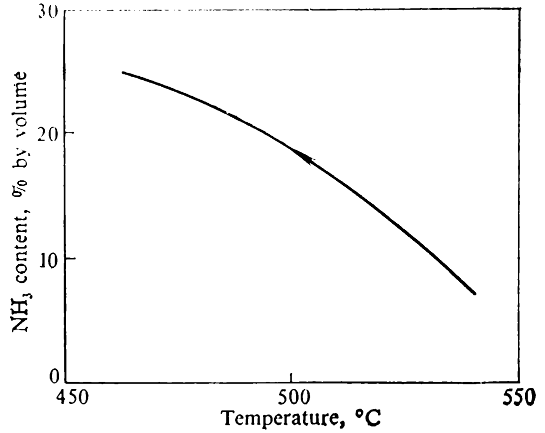


Fig. 56. The optimal temperature condition for the ammonia synthesis reaction (the course of the process is indicated by the arrow)

The ammonia synthesis rate also depends on the volume rate of the gas (the amount of the gas in cubic metres passing through 1 m^3 of the catalyst per hour, $m^3/m^3 \cdot h$). Table 7 presents the data on the effect of the volume rate on the ammonia concentration in the synthesis gas at a pressure of 300 kgf/cm^2.

It is clear from Table 7 that as the volume rate increases or as the time of contact of gas particles with the catalyst

TABLE 7. The Ammonia Concentration in the Synthesis Gas Depending on the Volume Rate

Volume rate, $m^3/m^3 \cdot h$	NH_3 content (%) at different temperatures, °C		
	450	475	500
15 000	19.6	21.6	23.0
30 000	14.6	17.7	18.2
45 000	12.7	15.2	16.5

is reduced, which is the same thing, the ammonia concentration decreases in the gas. However, it is very important that this reduction is not proportional to an increased volume rate. For example, as the volume rate increases from 15 000 to 45 000 $m^3/m^3 \cdot h$ (i.e. three-fold) the ammonia concentration decreases from 19.6 to 12.7 per cent at 450 °C, i.e. by as little as 6.9 per cent. Hence, as the volume rate increases, the amount of ammonia produced per unit of the catalyst volume should increase. In fact, in the first case, the amount of NH_3 produced from 1 m^3 of the catalyst per hour is $15\,000 \times 0.196 = 2850$ m^3, and in the second case, $45\,000 \times 0.127 = 5715$ m^3. Thus, an increase in the volume rate from 15 000 to 45 000 $m^3/m^3 \cdot h$ resulted in increasing the catalyst intensity two-fold. Hence, the conclusion can be made that it is desirable to operate catalytic reactors at high volume rates.

In modern ammonia synthesis plants the volume rate is 30 000 $m^3/m^3 \cdot h$. At higher volume rates, when large amounts of the gas pass through the catalyst, heat evolution, according to reaction (7.12), may not be sufficient to maintain the synthesis temperature at about 500 °C. In addition, an increase in the volume rate is accompanied by a higher power consumption for gas transfer, and larger-size apparatus require higher metal consumption.

However, even if these synthesis conditions, such as high temperature, pressure, volume rate, and presence of a catalyst, are observed, nitrogen and hydrogen do not fully react. The gas mixture flowing out of the catalytic reactor contains as low as 18 to 20 per cent of ammonia, and the balance is the unreacted nitrogen-hydrogen mixture. The problem arose how to use the unreacted nitrogen-hydrogen mixture. The procedure is as follows: the gas mixture is cooled, ammonia being liquefied, and the nitrogen-hydrogen mixture is passed through the same catalytic reactor, i.e. the process is carried out according to a cyclic diagram.

Implementing ammonia synthesis in practice required an immense, joint effort of scientists and engineers. A number of highly complex problems had to be solved. They related to using high temperatures and pressures, seeking for active and cheap catalysts, and creating new types of chemical apparatus. These problems have been successfully solved by scientists. They not only served as the basis for creating the nitrogen industry, but also gave impetus to developing other chemical industries. The experience gained in the nitrogen industry had been used to create the processes to manufacture alcohols, organic acids, synthetic fuels, and other products.

Up to the present time the industrial synthesis of ammonia remains one of the advanced processes of chemical technology. Here assemblies with high, united power work. They make it possible to manufacture 1360 tons of ammonia daily in one catalyst reactor (synthesis column). In this case, the technological process is carried out according to energy-technological diagrams. They allow carrying out the process without any external electric power consumption due to utilizing the heat of chemical reactions.

Industrial processes of ammonia synthesis. Industrial plants for ammonia synthesis operate at different pressures. Depending on the pressure employed, there are low (100 kgf/cm^2), mean (200 to 550 kgf/cm^2), and high (600 to 1000 kgf/cm^2) pressure systems.

In every plant the resultant ammonia is separated by cooling the gas. Gaseous ammonia is transformed into a liquid. The temperature needed to cool the gas and to make liquid ammonia depends on pressure. The lower the pressure, the lower the temperature required to recover ammonia. For example, at a pressure of 1000 kgf/cm^2, the gas is cooled to 40 °C, and at a pressure of 100 kgf/cm^2, the temperature of about minus 60 °C is required. The use of high pressure makes it possible to accelerate the reaction and reduce the size of the apparatus. Thus, the use of high pressure has a number of advantages. However, higher pressure is accompanied by higher power consumption to compress the gas, and the apparatus wears out in a shorter period of time.

In view of this fact, mean pressure plants have found the most extensive applications. They are used to recover ammonia effectively and obtain a high synthesis rate. Therefore, only the diagram for ammonia synthesis at mean pressures will be discussed.

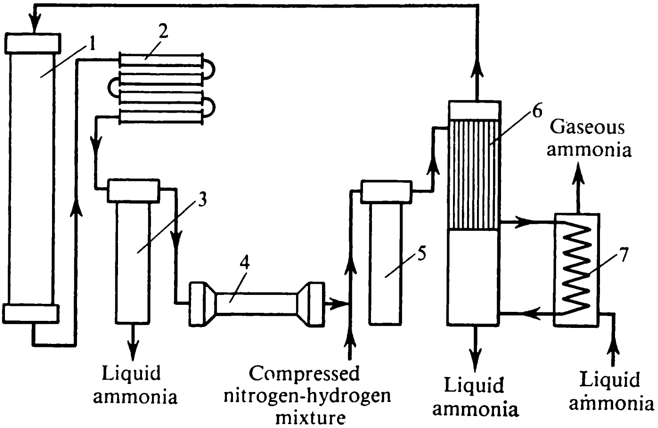


Fig. 57. Diagram of ammonia synthesis

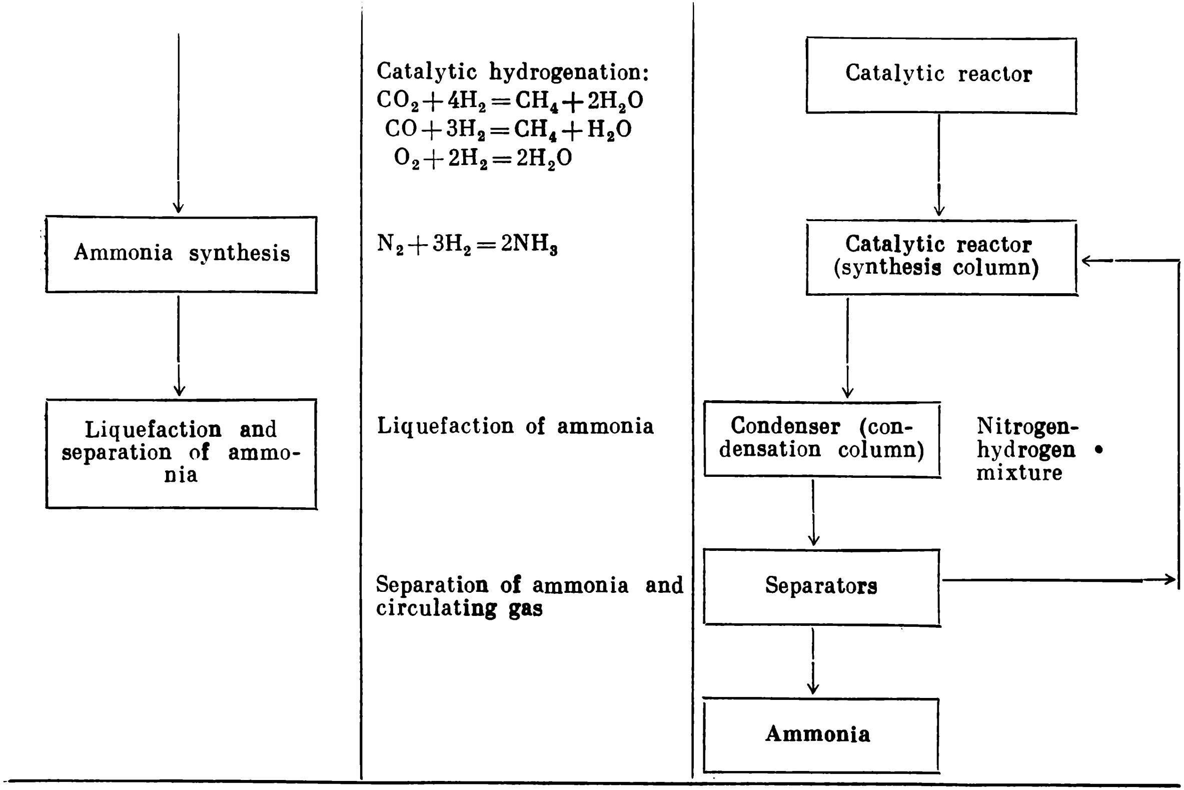
1—ammonia synthesis column; *2*—water condenser; *3*—separator; *4*—circulating pump; *5*—filter; *6*—condensation column; *7*—evaporator

The schematic diagram of ammonia synthesis at mean pressures is shown in Fig. 57. The gas mixture containing ammonia and unreacted nitrogen and hydrogen flows out of synthesis column *1* at a temperature of 200 °C. It is then admitted to water condenser *2* where part of ammonia is condensed and recovered in separator *3*.

The nitrogen-hydrogen mixture having traces of ammonia is then admitted to circulation pump *4*. The latter is used to circulate the gas in the synthesis plant. Before filter *5*, a fresh compressed nitrogen-hydrogen mixture is added to the circulating gas.

TABLE 8. **Manufacture of Ammonia**

Process	Operations	Apparatus employed
Preparation of nitrogen-hydrogen mixture	Methane conversion: $CH_4+H_2O=CO+3H_2$ $CH_4+0.5O_2=CO+2H_2$	Natural gas Steam Air Methane converter
	Carbon monoxide conversion $CO+H_2O=CO_2+H_2$	Steam Carbon monoxide converter
Purification of nitrogen-hydrogen mixture	Washing of synthesis gas with monoethanolamine solution: $2RNH_2+H_2O+CO_2=$ $=(RHNH_2)_2CO_3$	Packed towers


Ammonia synthesis
Liquefaction and separation of ammonia
Catalytic hydrogenation:
$CO_2+4H_2=CH_4+2H_2O$
$CO+3H_2=CH_4+H_2O$
$O_2+2H_2=2H_2O$
$N_2+3H_2=2NH_3$
Liquefaction of ammonia
Separation of ammonia and circulating gas
Catalytic reactor
Catalytic reactor (synthesis column)
Condenser (condensation column)
Nitrogen-hydrogen mixture
Separators
Ammonia

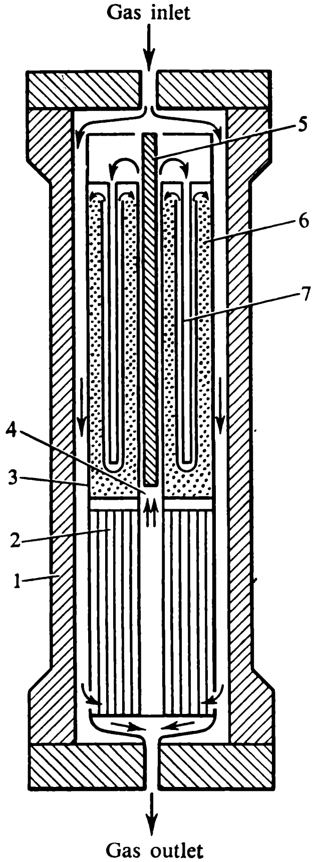


Fig. 58. Ammonia synthesis column

1—thick-walled cylinder; *2*—heat exchanger; *3*—catalyst box; *4*—central pipe; *5*—electric preheater; *6*—catalyst; *7*—heat exchange tubes

A mixture of the fresh and circulating gas in filter *5* is cleaned of the lubricating oil which may contaminate the catalyst. It is then fed to the secondary ammonia condensation system consisting of condensation column *6* and liquid ammonia evaporator *7*. In condensation column *6* the gas is cooled in the heat exchanger at the top of the column and is then directed to evaporator *7*. The nitrogen-hydrogen mixture is again cooled with evaporating liquid ammonia in this evaporator and is admitted to the bottom of column *6* which acts as a separator.

After separating the ammonia, the nitrogen-hydrogen mixture cools the gas in the heat exchanger. The gas is fed to the condensation column. From the condensation column the nitrogen-hydrogen mixture is directed to synthesis column *1*. Thus, the gas mixture is circulating through the same catalytic reactor. This allows the nitrogen-hydrogen mixture to be used effectively.

If ammonia is synthesized at a pressure of 450 kgf/cm^2 or higher, there is no need for secondary ammonia condensation, since, as a result of condensation, some ammonia remains in the gas when water cooling is employed.

The ammonia synthesis column is the main apparatus in ammonia manufacture. It is a complex structure operating at high temperatures and pressures. Much effort had been made to design the industrial apparatus. A great number of versions were rejected before scientists adopted the modern design of the ammonia synthesis column.

The shell of the synthesis column (Fig. 58) is made from high-strength steel, in the form of thick-walled cylinder *1*, 12 to 20 m high and about 1000 to 1400 mm in diameter. The column is closed tightly with covers at the top and bottom. The column interior accommodates heat exchanger *2* and catalytic box *3* into which a catalyst is charged.

A nitrogen-hydrogen mixture at a temperature of 20 to 30 °C is admitted to the top of the column, flows down along the circular space between the column walls and the catalyst box, and enters the bottom of heat exchanger *2*. The gas flows up the intertube space and is heated by the heat of the unreacted gases which are flowing down inside the heat exchanger tubes. From the heat exchanger the preheated gas is admitted to catalyst box *3*. The gas flows along central tube *4* which accommodates electric heater *5* that is switched on when the column is put into operation. To maintain the desired temperature at catalyst *6* and prevent it from overheating, double heat exchanger tubes *7* are immersed into the catalyst bed. First, the gas passes down along the narrow internal tube and then flows up along the circular space between the narrow and the wide tube. The gas removes the heat evolved at the catalyst, when nitrogen is reacted with hydrogen, becoming heated and is admitted onto the catalyst. The temperature rises to about 500 °C from the heat of synthesis. The reacted gases are directed from the catalyst to heat exchanger tubes *2*, where the heated gas is used to preheat a fresh gas, and they are then withdrawn from the ammonia synthesis column.

The main stages in the manufacture of ammonia from natural gases are shown in Table 8.

7.7 Grades of Ammonia, Its Transportation and Storage

According to GOST 6221-70, two grades of synthetic liquid ammonia are manufactured. They should meet the requirements set out in Table 9.

Liquid ammonia is kept at a pressure of 16 kgf/cm^2 at

TABLE 9. **Grades of Synthetic Ammonia**

Grade	Content			
	Ammonia, %	Water, %	Lubricating oil, mg/litre	Iron, mg/litre
1st	At least 99.9	Not more than 0.1	Not more than 10	Not more than 2
2nd	At least 99.6	Not more than 0.4	Not more than 35	—

storage sites in tanks and cylindrical vessels having a capacity of 50 to 100 m^3.

Liquid ammonia is carried in tank cars, tank trucks, and steel bottles. Ammonia tanks are painted white and have a yellow band on the side surface bearing the captions "Liquid Ammonia" and "Noxious Gas". Ammonia bottles are painted yellow with a black caption "Ammonia". Bottles filled with ammonia should not be kept in the sun or placed close to heat sources.

Perspectives of the Development in the Ammonia Manufacture

Large-capacity systems are now being developed. Large plants having a daily capacity of 1360 tons of methane are now the standard. This tendency of development indicates that the method for manufacturing ammonia from elements will retain its significance as one of the basic elements in the world's chemical industries to the end of the 20th century.

Yet, the major future problem will be to seek new methods for fixing nitrogen. The following trends may be singled out among the most interesting ones: the combustion of natural gases in the air when atmospheric nitrogen is oxidized by 1 or 2 per cent to nitric oxide; the production of nitric oxide from the air at high temperatures (the plasmochemical method makes it possible to fix up to 3 per cent of nitrogen); and fixing atmospheric nitrogen with tuber bacteria living on bean plant roots under artificial process conditions.

REVIEW QUESTIONS

1. Name the natural sources of free (unfixed) nitrogen and nitrogen fixed into chemical compounds.
2. What are the advantages of ammonia synthesis as compared with other methods for manufacturing nitrogen compounds from atmospheric nitrogen?
3. What phenomenon is air separation based on?
4. Name the basic industrial methods for manufacturing hydrogen.
5. Under what conditions does carbon monoxide conversion occur?
6. How is methane conversion effected? What catalytic reactor is used for this purpose?
7. What impurities are converted gases cleaned from?
8. How is hydrogen manufactured from coke-oven gases?
9. How do pressures and temperatures affect the ammonia synthesis process?
10. Why is a cyclic production adopted in ammonia synthesis? Draw the diagram.
11. How is an ammonia synthesis column designed?
12. What purposes are synthetic ammonia used for?

Chapter 8

MANUFACTURE OF NITRIC ACID

8.1 Properties and Grades of Nitric Acid

Nitric acid is one of the most important mineral acids. Anhydrous nitric acid, HNO_3, is a colourless heavy liquid with a density of 1.52 g/cm^3 (at 15 °C). It fumes in the air. Its freezing point is —47 °C and boiling point, 86 °C. Acid boiling is accompanied by acid partial decomposition and nitrogen dioxide evolution. While being dissolved in the acid, the evolving nitrogen dioxide tints it yellow or red (depending on the amount of NO_2). As the dilute nitric acid evaporates, its content in the solution increases to 68.4 per cent.

Nitric acid is a strong oxidizing agent. Concentrated nitric acid converts most metals to the corresponding oxides and nitrates. When some metals, such as Al, Fe, and Cr react with nitric acid, a layer of oxides resistant to the acid action is formed on their surfaces.

When subjected to the action of nitric acid, many organic compounds are decomposed. When contacted with concentrated nitric acid, some compounds may ignite. When reacted with cyclic organic compounds, concentrated nitric acid replaces the hydrogen atoms by the nitro group in these compounds. Nitric acid forms ethers with hydroxyl-containing organic compounds.

Nitric acid is widely used both in the chemical and other industries. It is second in industrial output preceded only by sulphuric acid. The greater part of nitric acid is used to manufacture fertilizers, explosives, and propellants. Besides, nitric acid is employed to manufacture sulphuric acid (the nitrous method), synthetic dyes, plastics, synthetic fibres, etc.

TABLE 10. **Grades of Nitric Acid**

Nitric acid	HNO_3 content, % by mass	Nitric acid	HNO_3 content, % by mass
Weak		*Concentrated*	
Grades:		Grades:	
1st	55	high-quality	98.9
2nd	47	1st	98.5
3rd	45	2nd	97.5

Three grades of dilute (weak) and two grades of concentrated nitric acid are manufactured industrially (Table 10).

8.2 Manufacture of Weak Nitric Acid

Until the twenties of this century, nitric acid had been manufactured from Chilean saltpeter by reacting it with sulphuric acid:

$$NaNO_3 + H_2SO_4 = HNO_3 + NaHSO_4 \qquad (8.1)$$

Saltpeter was decomposed by sulphuric acid in iron retorts heated with flue gases. The nitric acid vapours evolved were condensed in a cooler. 95-97%* sulphuric acid and 96% saltpeter produced 96-98% nitric acid.

Advances in ammonia synthesis from elements have made ammonia the basic source for the manufacture of nitric acid.

The first plant for the manufacture of nitric acid from ammonia was put into operation in Germany in 1909. However, due to inadequate technology, that plant followed by the others proved unprofitable.

In Russia I. Andreev, an engineer, and his co-workers did thorough research into this process in 1914-1916. The research results proved so fruitful that they laid the foundation for the construction of Russia's first plant for the manufacture of nitric acid.

Ammonia is turned into nitric acid by oxidizing it with atmospheric oxygen according to the following reaction:

$$4NH_3 + 5O_2 = 4NO + 6H_2O + 910\ \text{kJ} \qquad (8.2)$$

The resulting nitric oxide is a colourless gas which is readily oxidized to nitrogen dioxide:

$$2NO + O_2 = 2NO_2 + 124\ \text{kJ} \qquad (8.3)$$

Nitrogen dioxide is a heavy brown suffocating gas. When dissolved in water, it produces nitric acid:

$$3NO_2 + H_2O = 2HNO_3 + NO + 137\ \text{kJ} \qquad (8.4)$$

As is evident, the process for producing nitric acid is comprised of a number of consecutive stages. Reaction (8.2) describes the first stage, i.e. the oxidation of ammonia. The resultant gases, which include nitric oxide, are called nitrous gases. The second stage is described by reactions (8.3) and (8.4) and processes nitrous gases into nitric acid.

The Oxidation of Ammonia. The process occurs at a sufficient rate only at high temperatures. In addition to reaction (8.2), other reactions also occur:

$$4NH_3 + 4O_2 = 2N_2O + 6H_2O + 1108\ \text{kJ} \qquad (8.5)$$

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O + 1273\ \text{kJ} \qquad (8.6)$$

Reactions (8.5) and (8.6) produce nitrous oxide and nitrogen from ammonia instead of the desired nitric oxide. Hence the process conditions should be such when the basic (desired) reaction (8.2) would occur at a considerably higher rate than that in reactions (8.5) and (8.6).

As the temperature rises to 800 °C, the desired reaction rate increases much more than the rates of side reactions, and therefore the yield of the desired product—nitric oxide—increases. Higher temperatures cause decomposition of ammonia to nitrogen, and also the nitric oxide resulting from reaction (8.2) to nitrogen and oxygen, and the yield of nitric oxide decreases (Fig. 59). The ammonia oxidation process is therefore carried out at a temperature of about 800 °C. However, even in these conditions, a catalyst should be present. The process does not proceed in the desired direction if no catalyst is present.

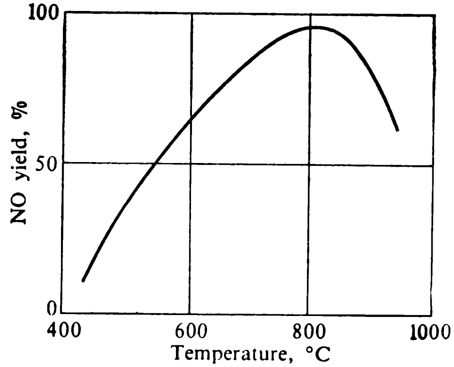


Fig. 59. The temperature dependence of nitric oxide yield during ammonia oxidation

To oxidize ammonia, an expensive catalyst, platinum alloyed with rhodium or palladium, is used. This catalyst has not, up to the present time, been surpassed by any other. Cheaper catalysts proved to be less active and stable. Platinum catalysts are manufactured in the form of gauzes from very thin wire of 0.06 to 0.09 mm in diameter. 1 cm^2 of the gauze has 1024 holes through which an ammonia-air mixture passes.

The direction of the process towards reaction (8.2) also depends on the time of contact of the ammonia-air mixture with the catalyst (the contact time). A contact time of 0.0001 to 0.0002 s proved to be highly advantageous. If the contact time of the gas is shorter, i.e. if the gas stream flows at a higher rate, ammonia is not oxidized and the yield of nitric oxide decreases. If the contact time is longer, side reactions occur; this, in turn, reduces the yield of nitric oxide (Fig. 60).

An increase in pressure in the ammonia oxidation process promotes a higher reaction rate, but simultaneously results in greater platinum losses.

According to reaction (8.2) five oxygen molecules should be consumed per four ammonia molecules, i.e. 1 mole of NH_3 per 1.25 moles of O_2. To increase the oxidation rate and the yield of nitric oxide, 1 mole of ammonia is used per 1.7 to 2 moles of oxygen, this corresponds to about a 10-12% ammonia concentration in the ammonia-air mixture (Fig. 61). The oxygen that did not enter into reaction (8.2) is used to process nitrous gases to oxidize nitric oxide to nitrogen dioxide according to reaction (8.3).

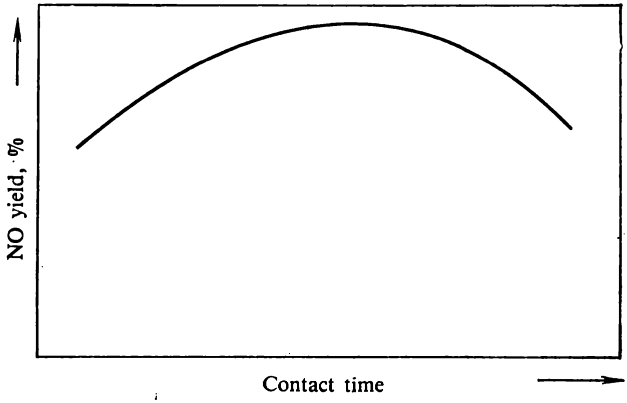


Fig. 60. The dependence of nitric oxide yield during ammonia oxidation on contact time

When making ammonia-air mixtures, it should be kept in mind that mixtures with a certain ammonia content are explosive. As can be seen from Fig. 62, about 16 to 28% ammonia concentrations at 18 °C are considered to be explosive.

In industry, it is common practice to handle ammonia-air mixtures having the ammonia content which is outside the explosive concentrations.

The presence of some impurities in ammonia-air mixtures poisons catalysts. These impurities include hydrogen phosphide, sulphur compounds, dust, rust, and lubricating oil vapours. To prevent them settling onto the catalyst, air is supplied to the shop along an intake installed outside the plant, and thoroughly cleaned. To purify the gas from suspended impurities, porous porolite (ceramic) tubes are installed in front of the catalyst inside the catalytic reactor. Gas is filtered through the pores of these tubes.

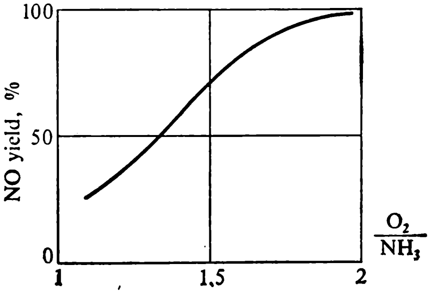


Fig. 61. The dependence of nitric oxide yield during ammonia oxidation on the O_2 : NH_3 ratio in the original mixture

The catalytic reactor for ammonia oxidation (Fig. 63) is a cylindrically shaped casing *1* with a catalyst package of platinum-rhodium gauzes *2* and porolite tubes *3*. An ammonia-air mixture is fed from the bottom of the reactor, filtered through the pores of tubes *3*, and passes consecutively through all the gauzes. The nitrous NO-containing gases are withdrawn from the top of the reactor. Plants operating at atmospheric pressure have a package that generally includes 3 or 4 gauzes, and at elevated pressures, 12 to 20 gauzes.

Processing Nitrous Gases into Nitric Acid. Reactions (8.3) and (8.4) occur in the same catalytic reactor. The nitric oxide resulting from reaction (8.4) is again oxidized to nitrogen dioxide which is then absorbed by water according to reaction (8.4), and so on. Reaction (8.3) is the slowest reaction among those reactions that occur when processing nitrous gases, which fact makes it responsible for the overall reaction rate. This makes it necessary to determine conditions under which nitric oxide will be intensively oxidized to nitrogen dioxide so as to attain a high processing rate.

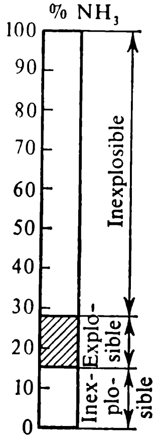


Fig. 62. Explosibility limits of ammonia-air mixtures (18 °C)

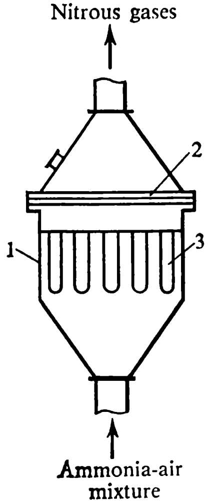


Fig. 63. Catalytic reactor for ammonia oxidation

1—base; *2*—catalyst; *3*—porolite tubes

The oxidation of NO to NO_2 occurs with a reduced volume. According to the Le Chatelier principle, the reaction equilibrium can be shifted from the left to the right, by increasing pressure. Higher pressure not only shifts the equilibrium of this reaction, but also accelerates it. Therefore, at plants operating at a pressure of about 10 kgf/cm^2, nitric oxide is practically completely oxidized to nitrogen dioxide.

Reaction (8.3) evolves heat. Therefore, to shift the equilibrium, the process should be carried out at low temperatures. As is known, a higher temperature enhances the rate of most reactions. However, the reaction of oxidation of nitric oxide to nitrogen dioxide is a rare exception; the reaction rate increases as the temperature lowers. Hence, to shift the equilibrium and to accelerate reaction (8.3), the process should be carried out at low temperatures.

Absorption of nitrogen dioxide by water is the final stage in the manufacture of nitric acid. During absorption the nitric acid concentration becomes higher. This process, as well as the oxidation of nitric oxide, requires that the temperature should be lowered and the pressure increased.

Processing nitrous gases, if the process is carried out at atmospheric pressure, produces nitric acid having a concentration of 48 to 50 per cent. An elevated pressure of about 10 kgf/cm^2 makes it possible to produce nitric acid having a concentration of 60 to 62 per cent or higher.

Flow Diagrams for Dilute Nitric Acid. Depending on the pressure, plants that manufacture a dilute nitric acid are classified into (1) those operating at atmospheric pressure; (2) those operating at elevated pressures; and (3) combined plants, where ammonia oxidation occurs at atmospheric pressure, and nitric oxide oxidation and nitrogen dioxide absorption by water occur at elevated pressures.

The flow diagram for the manufacture of a weak nitric acid at atmospheric pressure is shown in Fig. 64. The cleaned air and ammonia are admitted into mixer *1* at a ratio so as to produce an ammonia-air mixture having an NH_3 content of 10 to 12 per cent. From mixer *1*, the mixture is directed to catalytic reactor *2*, which accommodates platinum-rhodium gauzes.

The temperature of nitrous gases at the reactor outlet is maintained at about 800 °C. The oxidation level of ammonia to nitric oxide is about 97 or 98 per cent. In waste-heat boiler *3* the gas temperature is reduced to 250 °C. The gases are then cooled to 30 °C with water in case-tubular cooler *4*, water vapour is partially condensed and nitric oxide is oxidized to nitrogen dioxide. Therefore, weak nitric acid is partially formed in the cooler. The acid is fed to spray towers *5*. The absorption section comprises water (also called acid) absorption towers *5*, oxidation tower *6*, and absorption tower *7*. The gases leaving the cooler are passing consecutively through the towers. Six to eight towers connected in series are generally installed for water absorption, and two towers, for alkali absorption.

Water required for the absorption of nitrogen dioxide is fed to tower *5*, which is the last tower the gases are passed through. The resulting acid is transferred consecutively through all the towers by pumps *9*. The resulting 50% nitric acid is withdrawn from the tower that is the first tower the gases are passing through. About 92 per cent of nitric oxides are made into nitric acid in water absorption towers *5*. Oxidation tower *6* is installed behind the water absorption towers. The nitrous gases pass through the oxidation tower and are admitted into alkali absorption tower *7* to be absorbed with a soda solution. The following reaction occurs:

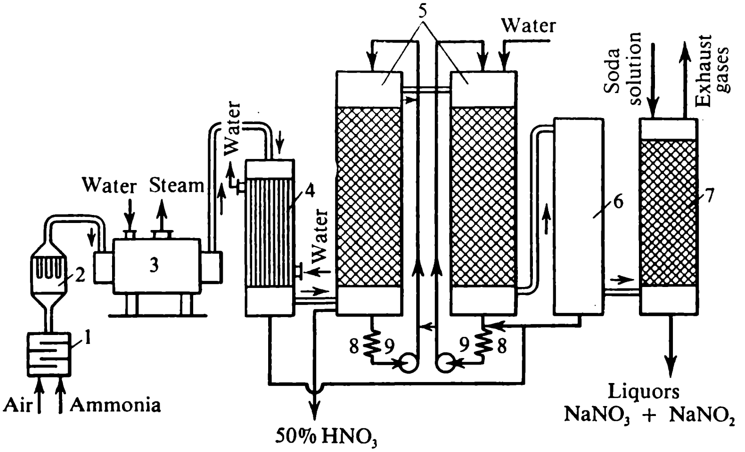


Fig. 64. Flow diagram for manufacturing dilute nitric acid at atmospheric pressure

1—mixer; *2*—catalytic reactor; *3*—waste-heat boiler; *4*—cooler; *5*—acid absorption towers; *6*—oxidation tower; *7*—alkali absorption tower; *8*—coolers; *9*—pumps

$$2NO_2 + Na_2CO_3 \rightarrow NaNO_3 + NaNO_2 + CO_2 \qquad (8.7)$$

The resulting solution containing sodium nitrate and sodium nitrite is treated with 50% nitric acid to evolve nitric oxide and to form sodium nitrate according to the following reaction:

$$3NaNO_2 + 2HNO_3 \rightarrow 3NaNO_3 + 2NO + H_2O \qquad (8.8)$$

The nitric oxide evolved is returned to the process for oxidation and absorption by water. The solution containing sodium nitrate is evaporated and sodium nitrate, which is used as a fertilizer, is crystallized.

The flow diagram for the manufacture of dilute nitric acid at elevated pressures of 8 to 10 kgf/cm^2 does not differ substantially from its manufacture at atmospheric pressure. However, plants operating at elevated pressures have a number of advantages, namely: the degree of nitric oxides processed into nitric acid increases to 98 or 99 per cent and the concentration of nitric acid being manufactured rises to 60 to 62 per cent; there is no need for alkali absorption; capital outlays for the construction of plants are cut down; and the consumption of special steel for the manufacture of apparatus is reduced, since the volume of absorption columns is many times less than in the systems at atmospheric pressure. At the same time, use of elevated pressures increases catalyst losses and power consumption; this is the disadvantage of these plants.

The manufacture of nitric acid at combined plants makes it possible to utilize the advantages of the both flow diagrams. Ammonia oxidation at atmospheric pressure allows reducing platinum losses as compared with those which cannot be avoided on elevated pressure plants. At the same time, processing of nitrous gases at elevated pressures makes it possible to manufacture 60 to 62% acid, eliminates the need for alkali cleaning, aids in reducing the outlays, and makes it possible to manufacture smaller-size apparatus. Nitric oxide absorption is effected at a pressure of 3 to 9 kgf/cm^2 at plants of this type. The combined plants are disadvantageous in that prior to absorption, very aggressive gases (nitrous gases) are subjected to compression. The principle of operation of a combined plant is shown in Table 11.

Powerful units having a daily capacity of 700 to 1200 tons of 100% nitric acid per day are now being introduced in industry on an ever growing scale. Some plants operate at a pressure of 3.5 or 4 kgf/cm^2 to oxidize ammonia, and at a pressure of 10 kgf/cm^2 or higher, to absorb nitric oxides. The heat liberated during ammonia oxidation and the heat liberated in the oxidation of NO to NO_2 are used to produce

TABLE 11. **Manufacture of Weak Nitric Acid**

Process	Operation	Apparatus employed
		Ammonia Air
Mixing		Mixer
Oxidation of ammonia	$4NH_3+5O_2=4NO+6H_2O$	Catalytic reactor
Compression of gases		Turbocompressor
Oxidation and absorption of nitric oxides	$2NO+O_2=2NO_2$ $3NO_2+H_2O=2HNO_3+NO$	Absorption columns
		60% nitric acid

electric power required for compressing air and nitrous gases to these pressures.

Modern high-capacity plants use considerably less power as compared with the other systems. The comparison of performance indices of various plants is shown in Table 12.

The data presented in Table 12 confirm the fact that elevated pressure plants, operating at smaller outlays as compared with atmospheric pressure plants, require higher consumption rates (for example, electric power and platinum).

The content of nitric oxides in the gases flowing out of the absorption columns amounts to 0.05 to 0.1 per cent. Since nitric oxides pollute the air basin, special "sanitary gas

TABLE 12. **Comparison of Methods for Manufacturing Nitric Acid**

Characteristic	Consumable coefficients per ton of HNO_3 for			
	atmospheric pressure plants	elevated pressure plants, $P=7\text{-}9$ kgf/cm^2	combined plants, $P=3.5$ kgf/cm^2 in absorption portion	high-capacity plants, $P=3.5\text{-}4$ kgf/cm^2; ammonia oxidation; $P=10$ kgf/cm^2 in absorption portion
Ammonia, ton	0.287-0.290	0.290-0.295	0.287-0.290	0.280-0.282
Platinum catalyst, g	0.045-0.049	0.155-0.170	0.045-0.049	0.09-0.100
Electric power, kW·h	115	360-380	230-260	8

cleaning" is required. The gases are heated to 380 to 480 °C, mixed with natural gas and directed to a reactor where nitric oxides are reduced to elementary nitrogen on a catalyst (palladium-coated alumina and active alumina). The content of nitric oxides is thus reduced to 0.004 to 0.006 per cent and the gases are discharged into the atmosphere through a 100 m pipe.

8.3 Manufacture of Concentrated Nitric Acid

Some industries require concentrated nitric acid having an HNO_3 content higher than 96 per cent. Nitric acid at this concentration can be manufactured by concentrating dilute nitric acid or by the direct synthesis method.

Concentration of Dilute Nitric Acid. To manufacture concentrated nitric acid dilute nitric acid is evaporated in the presence of sulphuric acid to remove water.

Figure 65 shows the schematic diagram of a plant for concentrating dilute nitric acid. Concentrated sulphuric acid is admitted to column *3* onto one of the top trays. Dilute nitric acid containing about 50 per cent of HNO_3 is admitted to the column slightly below. Part of the latter acid is evaporated and passed through evaporator *4*. Nitric acid vapours having insignificant amounts of water vapour and nitric oxides resulting from the decomposition of nitric acid are directed from column *3* to condenser *2* where the nitric acid is condensed, and the nitric oxides are trapped. Part of the nitric oxides are dissolved in the nitric acid, therefore, from condenser *2* the nitric acid is returned to the top column trays where it is purged with nitric acid vapours leaving the column, and then withdrawn into cooler *1* as the final product. The treated 70% dilute sulphuric acid flows from the bottom of the column and is admitted, without being cooled, for evaporation.

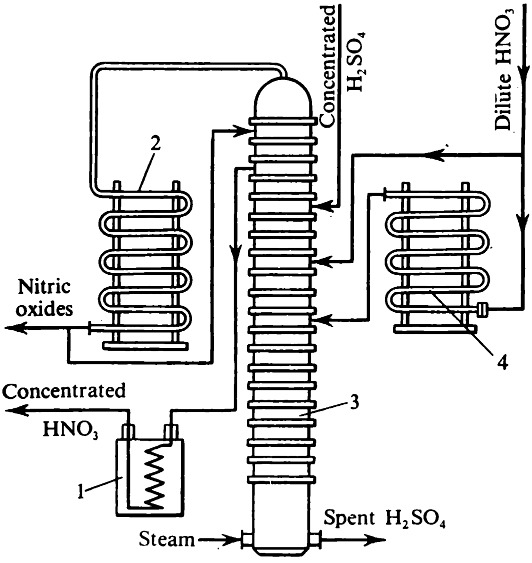


Fig. 65. Plant for manufacturing concentrated nitric acid

1—cooler; *2*—condenser; *3*—column; *4*—evaporator

Direct Synthesis of Nitric Acid. This method directly produces concentrated nitric acid from nitrous gases produced in the course of ammonia oxidation. The stages of the production of weak nitric acid, its concentration, and evaporation of sulphuric acid are eliminated.

The process is comprised of oxidizing nitric oxide contained in nitrous gases to nitrogen dioxide which, when cooled to about —8 °C, is converted to the liquid state to form N_2O_4.

Nitric acid is directly synthesized from liquid N_2O_4 when the latter reacts with water and oxygen:

$$2N_2O_{4\,\text{liq}} + 2H_2O + O_2 = 4HNO_3 \tag{8.9}$$

This reaction is carried out at a pressure of 50 kgf/cm^2 and a temperature of about 75 °C.

8.4 Storage and Transportation of Nitric Acid

A weak 45-60% nitric acid is kept in a storage site in reservoirs made from stainless steel. Small amounts of dilute nitric acid are carried in glass bottles which are packed into baskets or wooden bracing filled with shavings or straw impregnated with fireproof agents. Large amounts of dilute nitric acid are carried in tank cars made from stainless steel.

Concentrated nitric acid is stored in reservoirs and carried in tank cars made from aluminium.

REVIEW QUESTIONS

1. Name the basic users of nitric acid.
2. Write down the equations of reactions occurring during ammonia oxidation.
3. Draw the schematic of a catalytic reactor.
4. How do temperatures and pressure affect the oxidation of nitric oxide to nitrogen dioxide?
5. Describe the diagram to manufacture weak nitric acid as shown in Fig. 64.
6. What are advantages and disadvantages of nitric acid manufactured under elevated pressure?
7. What processes for producing concentrated nitric acid do you know?

Chapter 9

MANUFACTURE OF CALCINED SODA

9.1 The Importance of Soda for the National Economy

Several products are known as "soda" both in industrial and domestic applications: calcined soda is anhydrous sodium carbonate, Na_2CO_3 (the word "calcined" is derived from Latin meaning *fired* and *anhydrous*), sodium bicarbonate, $NaHCO_3$, often referred to as drinking soda; crystal sodium carbonate, $Na_2CO_3 \cdot 10H_2O$ and $Na_2CO_3 \cdot H_2O$; and caustic soda or sodium hydroxide, NaOH.

Calcined soda is very important for the chemical industry and other industries. It is widely used to manufacture soap, glass, iron-and-steel, petroleum, paint-and-varnish, textile, leather, and wood-pulp and paper, and in the food industry to produce many sodium salts, and to purify water (Diagram 10).

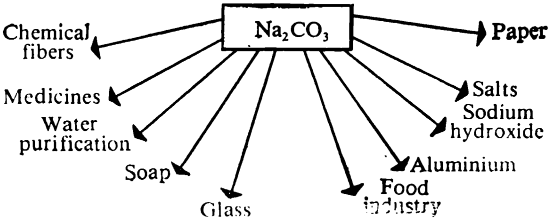


Diagram 10. Soda application

Drinking soda is used in the food, confectionery, chemical and pharmaceutical industries, and in medicine. Crystal sodium carbonate is predominantly used in the textile industry.

Only sal soda was used up to the end of the 18th century. Soda can be found naturally in solid form in small deposits, in solution it is found in the water of some soda lakes and alkali mineral springs.

By the end of the 18th century, when the shortage of soda and its high cost began to check the development of some industries, particularly the glass-making industry, it became necessary to find a method for producing artificial (synthetic) soda.

Synthetic calcined soda is now being consumed in almost every industry of the Soviet Union. The composition and the requirements for calcined soda are determined by GOST 5100-64, which sets the standard for Na_2CO_3 content to be at least 99 per cent.

The first process for manufacturing artificial soda in industry in 1891 was suggested by the French physician and chemist Leblan. This process manufactured soda from sodium sulphate, Na_2SO_4, lime, i.e. calcium carbonate, $CaCO_3$, and coal. Sodium sulphate was produced from solid common salt by reacting it with sulphuric acid:

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl \qquad (9.1)$$

The sodium sulphate was then fused with lime and coal at high temperatures in furnaces to produce a soda fusion cake:

$$Na_2SO_4 + CaCO_3 + 2C = Na_2CO_3 + CaS + 2CO_2 \qquad (9.2)$$

The resulting fusion cake was treated with water (leached). The leaching process gave a soda solution. The latter was evaporated to recover soda crystals. Following calcination of the crystals, the final product was formed.

Although in its time the Leblan process was considered a great engineering achievement, it had disadvantages. The calcined soda manufactured by this process was expensive and of poor quality. In addition, the process used bulky equipment. These drawbacks caused a more economical process to be looked for to manufacture soda.

When a more perfect ammonia process appeared in the mid-19th century, the Leblan process had lost its importance. The ammonia process for producing soda is now the basic method for manufacturing calcined soda in every country.

9.2 The Ammonia Process for Manufacturing Calcined Soda

Common salt, NaCl, as a saturated aqueous solution (brine) and limestone or chalk, $CaCO_3$, are the raw materials in the manufacture of calcined soda by the ammonia process. Ammonia is used as an adjuvant (hence the name of the process).

It is impossible to convert NaCl to Na_2CO_3 directly, since the ion of a strong hydrochloric acid cannot be replaced directly by the ion of a weak carbonic acid. Therefore, soda must be obtained through an intermediate compound.

Common salt is converted to soda by the exchange reaction that occurs in an aqueous solution between the two salts. It is known that this reaction yields two new salts. This reaction is a suitable process for producing salts, if one of the resulting salts is poorly soluble in water and can be precipitated from solution.

Soda, Na_2CO_3, is readily soluble in water. It is rather difficult to choose the products so that the second resulting salt will be insoluble. Therefore, soda is manufactured indirectly by first producing sodium bicarbonate, $NaHCO_3$, which is, unlike sodium carbonate, Na_2CO_3, slightly soluble in water. Its solubility becomes still lower in the presence of NaCl.

To produce sodium bicarbonate, the exchange reaction is carried out between the common salt present in the solution and soluble ammonium bicarbonate:

$$NaCl + NH_4HCO_3 \rightleftarrows \underset{\text{precipitate}}{NaHCO_3} + \underset{\text{solution}}{NH_4Cl} \qquad (9.3)$$

Ammonium carbonate is not manufactured separately, but results from the process itself by saturating the brine first with ammonia (ammonation of the solution), and then with carbon dioxide (carbonization of the solution). This is a complex process which may be presented by the following overall equation:

$$NH_3 + H_2O + CO_2 \rightleftarrows NH_4HCO_3 \qquad (9.4)$$

The reaction that produces sodium bicarbonate (9.3) is reversible, therefore it does not go to completion. It is impossible to convert all the common salt to bicarbonate. The conversion degree of common salt to bicarbonate depends on the temperature and the concentration of the reactants, and yields 70 to 75% in industrial conditions.

The resulting sodium bicarbonate is poorly soluble and is therefore recovered from solution in crystalline form. The

$NaHCO_3$ crystals are separated from the solution by filtration. The resulting sodium bicarbonate is converted to carbonate by calcination at high temperatures:

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O \quad (9.5)$$

This process is called calcination.

Thus, to manufacture calcined soda, the following operations should be performed: sodium bicarbonate is produced by saturating the common salt solution with ammonia and carbon dioxide, the resulting crystalline sodium bicarbonate is separated from the solution and then converted to carbonate by heating.

The production of sodium bicarbonate and carbonate is the basic process for manufacturing soda. In addition to this process, a number of auxiliary processes are carried out. They relate to the production of ammonia and carbon dioxide, which are essential for converting a solution of common salt to soda.

Carbon dioxide is derived by burning limestone or chalk:

$$CaCO_3 = CaO + CO_2 \quad (9.6)$$

(In addition to CO_2, this process produces burned lime, CaO, which also has found application in the manufacture of soda.) The evolved carbon dioxide is used to carbonize the brine. In addition, the carbon dioxide evolved during calcination is used for carbonization purposes.

Ammonia is produced by treating a solution of ammonium chloride, NH_4Cl. Ammonium chloride is formed when producing sodium bicarbonate according to reaction (9.3) and remains in solution after separation of the crystalline sodium bicarbonate. The solution is heated with lime milk (slaked lime, $Ca(OH)_2$, mixed with water). The ammonium chloride is decomposed and free ammonia evolves from the solution:

$$2NH_4Cl + Ca(OH)_2 = 2NH_3 + CaCl_2 + 2H_2O \quad (9.7)$$

The slaked lime, which is essential for this reaction, can be obtained by reacting burned lime, CaO (the calcined lime product), with water:

$$CaO + H_2O = Ca(OH)_2 \quad (9.8)$$

Decomposition of the ammonium chloride, reaction (9.7), evolves ammonia, which was used to produce sodium bicarbonate, and was converted to NH_4Cl according to reaction (9.3). Processes, in which the used-up reactant is recovered in original form, are called regeneration (recovery) processes. The regenerated ammonia is again used to saturate the brine (ammonation), i.e. ammonia passes through the production cycle, it reacts with common salt, carbon dioxide, and water to give ammonium chloride (reactions (9.3) and (9.4)). Then it is evolved by decomposing the ammonium chloride and enters into the reaction again. Therefore, the amount of ammonia throughout the entire production process should remain constant. However, due to imperfect apparatus or other reason, significant amounts of ammonia are lost. These losses are compensated by the addition of fresh ammonia.

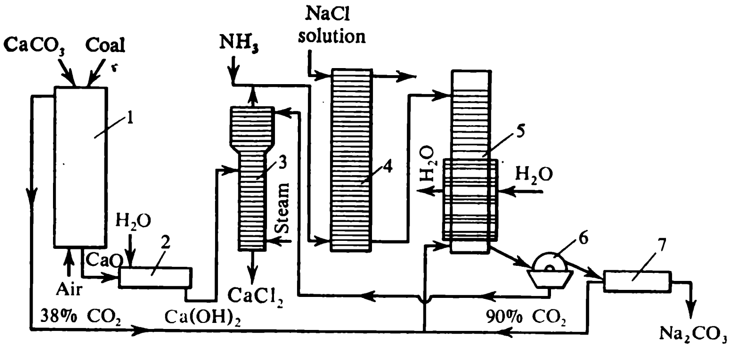


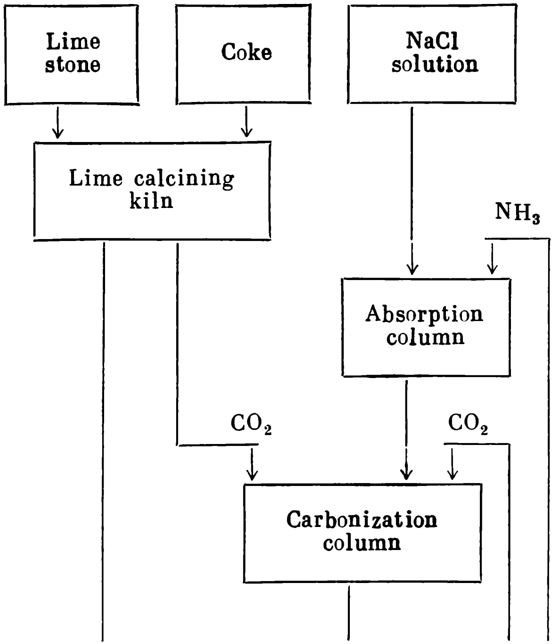
Fig. 66. Diagram for manufacturing calcined soda

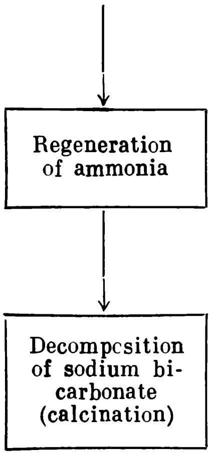
1—lime-calcining kiln; *2*—quencher; *3*—distillation column; *4*—absorption column; *5*—carbonation column; *6*—vacuum filter; *7*—drum-type kiln

These operations are summarized in Table 13. Figure 66 shows the schematic flow diagram for the manufacture of calcined soda by the ammonia method.

A common salt brine having a concentration of 300 g/litre is used to manufacture soda. In nature, brine is produced by underground leaching of common salt deposits. To do this, two pipes are inserted one into the other and are immersed

TABLE 13. Manufacture of Soda

Process	Operations	Apparatus employed
Manufacture of CO_2	$CaCO_3 = CaO + CO_2$	 Lime stone Coke NaCl solution Lime calcining kiln NH_3 Absorption column CO_2 CO_2 Carbonization column
Manufacture of sodium bicarbonate	Saturation of NaCl solution with ammonia Saturation of ammoniated solution with carbonic acid. Precipitation of crystals of sodium bicarbonate $H_2O + NH_3 + CO_2 = NH_4HCO_3$ $NH_4HCO_3 + NaCl = NaHCO_3 + NH_4Cl$	



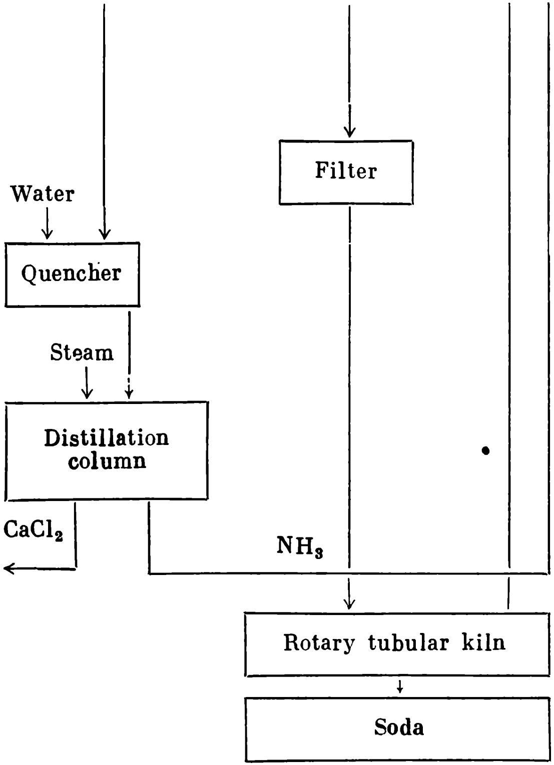
Filtration of $NaHCO_3$

$CaO + H_2O = Ca(OH)_2$

$2NH_4Cl + Ca(OH)_2 = 2NH_3 + CaCl_2 + 2H_2O$

Decomposition of sodium bicarbonate:

$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$



into a borehole (Fig. 67). Water, which dissolves the salts in the ground, is introduced under pressure through the inner pipe. The resulting brine is forced out by water along the outer pipe to the earth's surface. It is then collected in reservoirs and transferred to the plant along a pipeline.

In addition to NaCl, natural brine generally contains calcium and magnesium salts. During ammonation and carbonization of the brine, these impurities interact with NH_3 and CO_2 to cause precipitation, which will contaminate the equipment and disturb the normal course of the process. The brine is therefore precleaned to remove impurities. The impurities are precipitated by adding to the brine a strictly definite amount of reactants, such as a soda suspension in the cleared brine, and lime milk. This cleaning method is called the **soda-lime method.** The precipitated magnesium hydroxide, $Mg(OH)_2$, and calcium carbonate, $CaCO_3$, are separated in a settling tank.

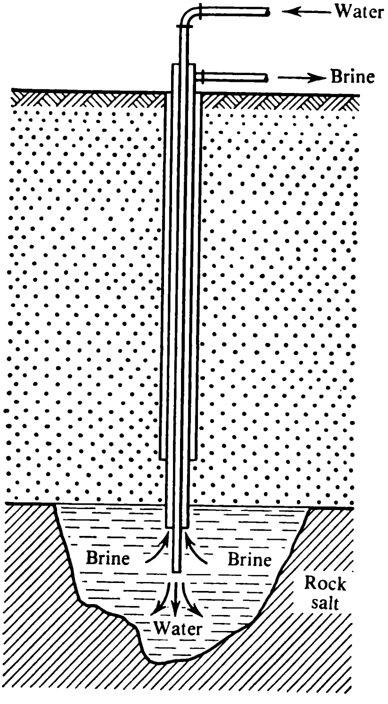


Fig. 67. Diagram of underground dissolution of salt

The cleaned and cleared brine of common salt is directed into absorption column *4* (Fig. 66) which is used to saturate the brine with ammonia (absorption), which is admitted from distillation column *3*. The absorption column (absorber) is essentially a bubble column. This type of column absorbs the gases with a liquid when gas pockets are bubbled through the layer of the liquid. Various devices are employed to break a jet into fine gas pockets and to increase the contact surface of the gaseous products with the liquid. The column intended to absorb the ammonia is comprised of several individual cast iron cylinders (casks) 2.8 m in diameter, fitted with bubble-cap trays. The total column height is about 30 m.

The operation of a single- and multibubble-cap trays is shown in Fig. 68. In the column the brine continuously moves downwards, flowing from one cylinder to the other along

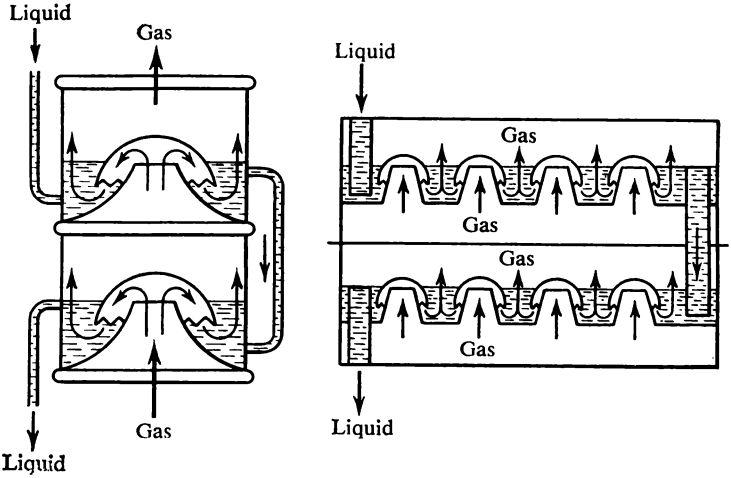


Fig. 68. Design and operation principle of single- and multibubble-cap trays

overflow pipes and the ammonia-containing gas is rising upwards to meet the brine that is running out, while bubbling from under the bubble caps.

The resulting ammoniacal brine is then directed to carbonization bubble column *5* (Fig. 66) in which the basic reaction (9.3) of conversion of the starting material to sodium bicarbonate, $NaHCO_3$, and ammonium chloride, NH_4Cl, occurs. Carbonic acid, which is required for this operation, is fed from a shaft-type kiln to burn limestone *1* and, from a drum-type kiln, to calcine bicarbonate *7*. Carbon dioxide is absorbed by the ammoniacal brine in a complex process that occurs in the carbonization column to form the sodium bicarbonate. This process is described by the following reactions (9.4) and (9.3):

$$NH_3 + H_2O + CO_2 \rightleftarrows NH_4HCO_3 + Q$$

$$NaCl + NH_4HCO_3 \rightleftarrows NaHCO_3 + NH_4Cl + Q$$

Ammonia and carbon dioxide react with a common salt brine with heat evolution; therefore the lower sections of columns *4* and *5* are provided with coolers into which cold water is fed.

Lower temperatures reduce the solubility of the sodium bicarbonate and shift the reaction equilibrium to the right. In this case, 70 to 75% of common salt is converted to $NaHCO_3$. The sodium bicarbonate formed in carbonization column *5*, being slightly soluble under process conditions, is found as fine crystals in the suspended state of the solution of ammonium chloride.

Carbonization column *5* operates on the same principle as absorber *4*. But unlike absorption columns, which employ multibubble-cap trays, the carbonization column uses single bubble-cap trays. This is the cause that $NaHCO_3$ precipitates in the carbonization column and may clog up small-section bubble caps.

The sodium bicarbonate crystals formed in the carbonization column are separated from the solution on drum vacuum-filter *6*. The filtrate produced in the vacuum filter (the filter liquid) is fed to distillation bubble column *3* called the distiller, to recover (regenerate) ammonia from the ammonium chloride. The filter liquid is treated with lime milk to do this:

$$2NH_4Cl + Ca(OH)_2 = 2NH_3 + CaCl_2 + 2H_2O$$

Steam is fed from the bottom to effect better distillation of ammonia into distillation column *3*. After being cooled, the regenerated ammonia is fed to the bottom of column *4*.

When soda is manufactured by the ammonia method, theoretically ammonia should not be consumed. However, it is practically impossible to completely recycle ammonia in the process. Therefore, ammonia losses are compensated by adding ammonia as ammoniacal water to distiller *3* or as gaseous ammonia from the distiller to absorber *4*.

The sodium bicarbonate crystals that are separated from the ammonium chloride solution are washed with water on vacuum filter *6* to remove completely the filter liquid from the bicarbonate. They are directed to calcining kiln *7* which is a steel drum externally heated with flue gases and rotating at 5 revolutions per minute.

Shaft-type lime calcining kiln *1* is used to produce carbon dioxide and burned lime. Decomposing limestone into carbon dioxide, CO_2, and burned lime, CaO, consumes heat (the process is endothermic). Therefore, coal and coke are fed together with limestone from the top of the kiln, and air from the bottom. Temperatures of 1100 to 1200 °C develop in the shaft-type calcining kiln due to the heat resulting from the combustion of a solid fuel. Such a temperature is required to decompose limestone.

After being washed with water, the gas from lime calcining kilns, which contains about 40% carbon dioxide, is directed into carbonization column *5*. The burned lime produced in kiln *1* is slaked with water in a slaker, rotary drum *2*. After filtering coarse suspended particles, the lime milk that was prepared in an apparatus provided with a stirrer and having a concentration of 270 to 308 g/litre, is fed into distiller *3* to recover ammonia from the filter liquid.

The calcium chloride, $CaCl_2$, solution left after evolution of ammonia and containing NaCl is withdrawn from distillation column *3*. This is a waste product of soda manufacture. It is directed to sludge basins, so-called "white seas", located outside the plant. This waste product has not, to date, found application, and the problem of its utilization remains unsolved.

9.3 Manufacture of Sodium Bicarbonate

Sodium bicarbonate, $NaHCO_3$—drinking soda—has found application in the food industry, medicine, etc. It has to meet high standards with respect to purity. Sodium bicarbonate is manufactured predominantly from an intermediate product of the basic production, such as crude sodium bicarbonate obtained in a vacuum filter. Crude sodium bicarbonate is placed in water producing a suspended pulp (the bicarbonate is poorly soluble in water). Steam is passed through the pulp to decompose the bicarbonate:

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O \qquad (9.9)$$

The soda solution thus formed is subjected to carbonization:

$$Na_2CO_3 + CO_2 + H_2O = 2NaHCO_3 \qquad (9.10)$$

The resulting pure sodium bicarbonate is filtered, dried, and packed into containers in dry rooms. It should contain at least 98.5% $NaHCO_3$ and not more than 1.0 to 1.2% Na_2CO_3, 0.05% NaCl and 1.0% H_2O. It should contain no arsenic, ammonium, and heavy metal salts.

9.4 Basic Trends in the Development of Soda Production

The production and consumption of calcined soda in the Soviet Union will grow with every passing year. This will undoubtedly result in changes both in the technological process and the apparatus employed. Even though ammonia production has found industrial application for over a hundred years, this method remains basically imperfect up to the present time. It has a low raw material utilization coefficient for both sodium and carbon dioxide. The chlorine, contained in the starting common salt, and lime are almost completely lost as waste products, such as calcium chloride.

The soda industry in the Soviet Union is improving the technological processes, intensifying apparatus operation, and mechanizing labour consuming processes, automating individual stages and the soda production as a whole. Measures are being taken to utilize the waste products of soda production, such as calcium chloride and fine fractions of chalk and limestone. A problem arises when manufacturing soda from natural sodium sulphate, mirabilite, how to produce simultaneously ammonium sulphate used as a fertilizer. It is proposed to manufacture soda without regenerating ammonia from the NH_4Cl solution, and to recover the ammonium chloride from the solution and use it as a fertilizer. The use of sylvinite ($KCl \cdot NaCl$) instead of sodium chloride is worthy of attention. This will make it possible to manufacture soda and nitrogen-potash fertilizers ($KCl + NH_4Cl$).

REVIEW QUESTIONS

1. Name the types of soda and their basic users.
2. Explain why it is not possible to manufacture soda from a common salt solution by merely exchanging it with carbon dioxide.
3. Explain what role is played by the regeneration of ammonia from ammonium chloride solutions. What is lime milk and how is it produced?
4. Name the sources of carbon dioxide used for the carbonization of brines.
5. Thermal decomposition of limestone evolves 100 per cent of CO_2. Why is it that lime calcining kilns produce a gas containing as little as 38-40 per cent of CO_2?
6. What method for increasing the contact surface of the reacting G-L system is used in the manufacture of soda?
7. Name the basic apparatus for the manufacture of calcined soda by the ammonia method.
8. What are the disadvantages of the ammonia method in the manufacture of calcined soda?
9. How is pure sodium bicarbonate manufactured?

Chapter 10

MANUFACTURE OF SODIUM HYDROXIDE, CHLORINE, AND HYDROCHLORIC ACID

Sodium hydroxide, NaOH, chlorine, and hydrochloric acid, HCl, are widely used in some industries.

Sodium hydroxide is a strong alkali, called caustic soda in everyday life. It is employed in soap making, in the manufacture of alumina which is an intermediate product in the production of metallic aluminium, in the paint-and-varnish, and petroleum refining industries, in the manufacture of rayon, in the organic synthesis industry, and in other industries of the national economy.

Chlorine is a yellow-green heavy gas with a suffocating odour at atmospheric pressure and normal temperature. Its boiling point is —33.6 °C and its freezing point is —101.5 °C. Chlorine is used to manufacture organic chloroderivatives, plastics, synthetic rubbers, chemical fibres, solvents, insecticides (agents for controlling agricultural pests), hydrochloric acid, sodium and calcium hypochlorites, NaClO and $Ca(ClO)_2$, chlorates, $NaClO_3$, etc. Chlorine is also used in metallurgy, the petroleum industry, for rendering harmless drinking and waste waters, in medicine and sanitary, and in pyrotechnics.

Hydrochloric acid is an aqueous solution of hydrogen chloride. Commercial hydrochloric acid contains 27.5 to 31 per cent of HCl. This acid has found application in the manufacture of inorganic salts of zinc, barium and other metals, nonferrous metallurgy, hydrolysis of starch, and in some other industries. Industrial hydrochloric acid of the 1st and 2nd grades and synthetic hydrochloric acid are manufactured. The HCl content should be at least 27.5 per cent in the industrial acid and 31 per cent in the synthetic acid.

Hydrogen chloride is a colourless gas having a melting point of —114.2 °C and boiling point of —85 °C. Dissolving hydrogen chloride in water produces hydrochloric acid. Hydrogen chloride is used to manufacture organic chloroderivatives, such as vinyl chloride, and ethyl chloride.

When working with chlorine, hydrogen chloride, hydrochloric acid, and sodium hydroxide, safety rules must be strictly observed. Inhalation of chlorine causes a sharp cough and suffocation, inflammation of the mucosas of the respiratory system, emphysema, and subsequently formation of inflammatory focal points in the lungs.

Despite an insignificant amount in the air, hydrogen chloride causes irritation in the nose and larynx, occasional pains in the breast, hoarseness and suffocation. When man is chronically intoxicated with small concentrations of hydrogen chloride, teeth are especially affected, and their enamel is rapidly destroyed. Hydrochloric acid poisoning is identical with chlorine poisoning.

10.1 Chemical Processes for Producing Sodium Hydroxide

Chemical processes for producing sodium hydroxide include lime and ferrite processes.

The lime process for producing sodium hydroxide is done by reacting soda solution with lime milk at a temperature of about 80 °C. This process is called causticization and is described by the following reaction:

$$Na_2CO_3 + Ca(OH)_2 = \underset{\text{solution}}{2NaOH} + \underset{\text{precipitate}}{CaCO_3} \qquad (10.1)$$

Reaction (10.1) produces a sodium hydroxide solution and a calcium carbonate precipitate. The calcium carbonate is separated from the solution which is evaporated to form a molten product containing about 92 per cent of NaOH. The molten NaOH is poured into iron drums where it cools.

The ferrite process is described by the two reactions:

$$Na_2CO_3 + Fe_2O_3 = \underset{\text{sodium ferrite}}{Na_2O \cdot Fe_2O_3} + CO_2 \qquad (10.2)$$

$$Na_2O \cdot Fe_2O_3 + H_2O = \underset{\text{solution}}{2NaOH} + \underset{\text{precipitate}}{Fe_2O_3} \qquad (10.3)$$

Reaction (10.2) shows the process of caking calcined soda with ferric oxide at a temperature of from 1100 to 1200 °C. In this case, a sodium ferrite cake is formed and carbon dioxide evolves. The cake is then treated (leached) with water according to reaction (10.3) to form a sodium hydroxide solution and a Fe_2O_3 precipitate. Then after this is separated from the solution, it is recycled. The solution contains about 400 g/litre of NaOH. The solution is evaporated to form a product containing about 92 per cent of NaOH.

Chemical methods for producing sodium hydroxide have substantial disadvantages, since large amounts of fuel are consumed, the resulting sodium hydroxide is contaminated with impurities, and servicing of the apparatus is a labour-consuming operation. At the present time, these processes have been almost completely replaced by the electrochemical production process.

10.2 The Electrochemical Process for Producing Chlorine, Sodium Hydroxide, and Hydrogen

The Concept of Electrolysis and Electrochemical Processes. Electrochemical processes are chemical processes that occur in aqueous solutions or melts when a direct electric current is applied.

Solutions and melts of salts, solutions of acids and alkalis called electrolytes are the 2nd type conductors in which an electric current is transferred by ions. (The 1st type, for example, metals, conduct electric current by electrons.) As electric current passes through the electrolyte, ions discharge on the electrodes and the appropriate substances are deposited. This process is called electrolysis. The apparatus in which electrolysis occurs is called an electrolytic cell or an electrolytic bath.

Electrolysis has found wide application in the chemical and other industries. When it is used to plate metallic articles with another metal, it is called electroplating. This is essential to protect metals from corrosion, to improve strength of articles, and so on.

Electrolysis is used in the manufacture of some chemical products, such as chlorine, hydrogen, oxygen and alkalis. It should be noted that electrolysis produces chemical products with a high degree of purity. In some cases, this cannot be done when products are manufactured by chemical processes. Light metals, such as magnesium and aluminium, and heavy metals, such as copper, zinc, nickel, and lead, are manufactured by industrial electrochemical processes. Thus, the assortment of electrolysis products is exceedingly great.

Electrochemical processes are disadvantageous in that electrolysis requires high power consumption. This increases the cost of the products obtained. In connection with this fact, it is advisable to use electrochemical processes only if cheap electric power is available.

An outstanding contribution to the development of electrochemical processes was made by Faraday when he formulated their basic laws.

Faraday's first law states that the amount of substance deposited on the electrode is directly proportional to the amount of electricity passing through the electrolyte. The amount of electricity is equal to the product of the current intensity and time, and is measured in ampere hours. If we denote the current intensity as I, and time as τ, the amount of electricity Q will be:

$$Q = I\tau \tag{10.4}$$

For example, if an electric current of 10 A passes through an electrolyte for 1 hour, it means that the total amount of electricity is equal to 10 A·h. If the current intensity is 100 A, and the electrolysis time is 0.1 hour, the amount of electricity will also be 10 A·h. Hence, the amount of electricity is equal in the first and second cases. According to Faraday's first law, the same amount of substance is deposited in both cases. If a current of 100 A passes through the electrolyte for 2 hours, the amount of electricity will be 200 A·h, and the amount of the substance deposited on the electrodes will be 20 times more than in the first two cases.

Faraday's second law states that as the same amount of electricity passes through solutions of various electrolytes, the amount of substances deposited on the electrodes is proportional to the gram-equivalents of these substances.

The gram-equivalent is the ratio of the atomic weight of a substance to its valence. For example, the gram-equivalent of silver is equal to $\frac{107.88}{1} = 107.88$ g; of divalent copper, $\frac{63.57}{2} = 31.78$ g, hexavalent chromium, $\frac{52.01}{6} = 8.66$ g.

Hence, according to Faraday's second law, if the equal amount of electricity passes through an electrolyte containing $AgNO_3$, $CuSO_4$, and $H_2Cr_2O_7$, the amount of silver, copper, and chromium deposited on the electrodes will be in the ratio of 107.88 : 31.78 : 8.66.

To obtain 1 g-equiv of the substance, theoretically it is necessary to consume 96 500 coul. This value is called the Faraday constant. Since 1 coul is equal to the amount of electricity that passes in 1 s at a current of 1 A, 96 500 coul will give 96 500 : 3600 = 26.8 A·h (3600 is the number of seconds in 1 hour). Hence, 1 g-equiv of the substance will be obtained for 26.8 A·h.

The amount of the substance obtained in 1 A·h will be 26.8 times smaller, i.e. 1 g-equiv: 26.8. This value is called the electrochemical equivalent. For example, the gram-equivalent is 35.46 g for chlorine, 40.0 g for sodium hydroxide, and 1.008 g for hydrogen. Accordingly, the electrochemical equivalent is 35.46 : 26.8 = 1.323 g for chlorine, 1.008 : 26.8 = 0.0376 g for hydrogen, and 40 : 26.8 = = 1.4926 g for sodium hydroxide.

The amounts of substances that are practically deposited on the electrodes are smaller than envisaged in Faraday's laws. This can be explained by the fact that in addition to the basic process which causes the required (desired) products to deposit on the electrodes, there are processes that cause by-products also to deposit. Current efficiency assesses the efficiency of an electrochemical process.

Current efficiency is the ratio of the amount of the substance deposited on the electrodes (G_a) to the theoretically possible amount (G_t), calculated according to Faraday's laws. Current efficiency η is generally expressed in per cent:

$$\eta = \frac{G_a}{G_t} \times 100\% \tag{10.5}$$

For example, a current of 100 A is passed through a nickel salt solution for 0.5 hour to form 50 g of nickel. The current efficiency should be determined. The atomic weight of nickel is 58.7 and its valence is 2.

According to Faraday's laws $\frac{58.7}{2 \times 26.8} = 1.095$ g of the substance will be deposited for 1 A·h.

Since a current of $100 \times 0.5 = 50$ A·h passed through the solution, the total amount of the deposited substance would be $1.095 \times 50 = 54.75$ g. Hence, the current efficiency will be:

$$\eta = \frac{50}{54.75} \times 100 = 91.3\%$$

This indicates that in addition to the basic process which requires electric power in electrolysis, other processes occur which also involve power consumption. The actual power consumed in electrolysis will be smaller, the lower the voltage applied to the electrolytic cell and the higher the current efficiency. **Power utilization factor** (μ) measures the power efficiency in electrolysis. This factor is the ratio of the energy required in theory to produce a unit of product (W_t) to the actual amount of energy consumed (W_a):

$$\mu = \frac{W_t}{W_a} \times 100\% \tag{10.6}$$

or

$$\mu = \frac{V_t}{V_a} \eta \tag{10.6a}$$

where V_t is the theoretical voltage applied to the electrolytic cell, V_a the actual voltage, and η is the current efficiency.

In practice, the power utilization factor should be as high as possible. This is accomplished when the voltage (V_a) applied to the electrolysis bath is low, and the current efficiency (η) is high.

The Raw Materials. To manufacture chlorine, sodium hydroxide, and hydrogen, a common salt solution is used which is subjected to electrolysis. Common salt occurs in nature as underground rock salt deposits, in the water of lakes and seas, and in the form of natural brines or solutions.

In summer time, water evaporates from the surfaces of lakes, and common salt precipitates as crystals. This is self-deposited salt. Sea water contains about 35 g/litre of sodium chloride. In hot climates where water evaporates quickly, concentrated solutions of sodium chloride are formed. Sodium chloride crystallizes from these solutions. Underground water flows in salt seams in the Earth. This water dissolves NaCl to form underground brines which rise to the surface through boreholes.

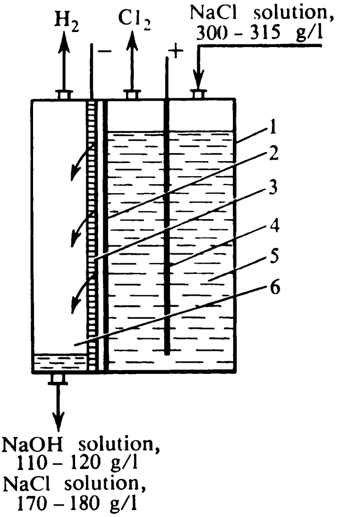

H_2
Cl_2
−
+
NaCl solution, 300 - 315 g/l
1
2
3
4
5
6
NaOH solution, 110 - 120 g/l
NaCl solution, 170 - 180 g/l

Fig. 69. Bath with filtering diaphragm

1—cylindrical vessel; *2*—asbestos diaphragm; *3*—iron cathode; *4*—graphite anode; *5*—anode space; *6*—cathode space

Electrolysis of Sodium Chloride Solutions. This process is carried out in baths with filter diaphragms and iron cathodes, and in baths with mercury-pool cathodes.

A bath with a filter diaphragm (Fig. 69) is vessel *1*. The interior accommodates asbestos diaphragm *2*, iron cathode *3* in the form of a gauze, and graphite anode *4*.

Sodium chloride dissociates into Na^+ and Cl^- ions in aqueous solutions. Although slightly, water dissociates into H^+ and OH^- ions. As direct current is passed, chloride ions discharge onto the anode to form gaseous chlorine molecules:

$$2Cl^- - 2e = Cl_2 \tag{10.7}$$

Hydrogen ions discharge on the cathode:

$$2H^+ + 2e = H_2 \tag{10.8}$$

and hydrogen evolves.

Hydroxyl and sodium ions form sodium hydroxide:

$$Na^+ + OH^- = NaOH \tag{10.9}$$

The sodium chloride solution (about 310 g/litre), which has been purified from calcium and magnesium ions, is fed to anode space *5* of the bath, where, as an electric current passes at a temperature of about 80 °C, chlorine evolves at the anode. The sodium chloride solution is filtered through diaphragm *2*, hydrogen evolves at the cathode and is removed from cathode space *6*. Together with the undecomposed common salt, the resulting NaOH runs to the bottom of the cathode space and is withdrawn from the bath. This solution is called an electrolytic liquor and is composed of the following constituents: 110 to 120 g/litre NaOH and 170 to 180 g/litre NaCl.

The surfaces of the cathode and diaphragm are designed to be as developed as possible, given the volume of the bath, so as to use the surface of the anode more fully to increase the load applied to the bath (the current intensity) and to improve its capacity. This makes the shape of the cathode more complicated, as the result of which it is more difficult to coat the cathode with asbestos board. In this case, a diaphragm is applied by filtering suspended asbestos fibre in the brine through the complicated surface of the cathode. These baths are called baths with deposited diaphragms. БГК-13 and БГК-17 baths with deposited diaphragms have been constructed in the Soviet Union. The operating characteristics of these baths are shown in Table 14.

Baths with mercury-pool (*liquid*) *cathodes* have two parts, an electrolytic cell and a decomposer, which are interconnected with each other (Fig. 70). Electrolytic cell *1* is a long

TABLE 14. **Operating Characteristics of Baths with Deposited Diaphragms**

Characteristic	Bath	
	БГК-13	БГК-17
Load, A	5000	20 000-30 000
Voltage, V	3.35	3.35-3.40
Current efficiency, %	93.5	94-96
Power consumption per ton of NaOH, kW·h	2370-2400	2350-2400
NaOH concentration, g/litre	120	135-140

closed box. Graphite anodes *2* are immersed into this box, and the cathode is mercury *3* which is flowing along the slightly inclined bath bottom. A 310 to 315 g/litre NaCl solution is continuously fed into the electrolytic cell. As direct current passes, chlorine deposits on the anode according to reaction (10.7), and sodium ions discharge on the cathode:

$$Na^+ + e = Na \qquad (10.10)$$

which react with mercury to form sodium amalgam:

$$Na^+ + nHg = NaHg_n \qquad (10.11)$$

The impoverished solution is continuously withdrawn from the electrolytic cell (it contains about 270 g/litre of NaCl) and sodium amalgam is admitted into decomposer *4* in which it is treated with water. The following reaction occurs:

$$NaHg_n + H_2O = NaOH + 0.5H_2 + nHg \qquad (10.12)$$

As can be seen from reaction (10.12), a sodium hydroxide solution and hydrogen are formed in the decomposer. The deposited mercury is returned to the electrolytic cell by pump *5*. Thus, the mercury flows in a closed cycle (electrolytic cell—decomposer—electrolytic cell). The impoverished sodium chloride solution is saturated with NaCl and again returns to the electrolysis process.

Baths with mercury-pool cathodes operate at a voltage of about 4.5 V. A current of 200 000 A is applied to the bath, and the electrolyte temperature varies from 70 to 80 °C, The current efficiency is from 94 to 96 per cent. The alkali concentration is 450 to 500 g/litre at the decomposer outlet, and the power consumed to manufacture 1 ton of NaOH varies from 3100 to 3200 kW·h.

Baths with mercury-pool cathodes are advantageous in that they produce high alkali concentrations, which reduces the fuel consumption for the evaporation of alkalis. Besides, these baths produce very pure alkalis. As compared with baths with filter diaphragms, these baths are disadvantageous in that they consume more power per unit of product, involve considerable capital outlays for the construction of baths, and large amounts of mercury are needed. In addition, harmful working conditions due to the presence of mercury vapours in the atmosphere at work premises are characteristic of operating these baths.

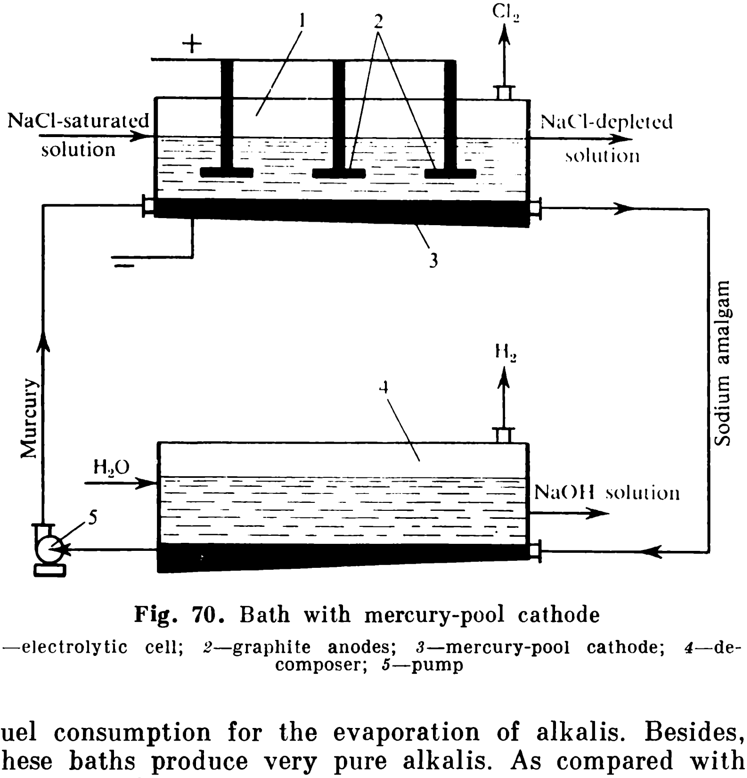


Fig. 70. Bath with mercury-pool cathode

1—electrolytic cell; *2*—graphite anodes; *3*—mercury-pool cathode; *4*—decomposer; *5*—pump

Despite the disadvantages of baths with mercury-pool cathodes, their use is growing. This can be attributed to the fact that some industries, like rayon manufacture, require pure alkalis containing no chlorides. This alkali can be obtained only in baths with mercury-pool cathodes.

Alkali solutions produced in baths with filter diaphragms and in the decomposers of baths with mercury-pool cathodes should be evaporated first in vacuum evaporators and then in boilers to obtain 92 to 94 per cent of NaOH. If liquors containing not only NaOH, but also NaCl are concentrated in baths with filter diaphragms, their evaporation causes sodium chloride to crystallize. However, NaCl cannot be removed completely, and therefore sodium hydroxide contains 2 or 3 per cent of NaCl. The sodium chloride that is liberated in the course of evaporation of liquors is returned to the electrolysis process (Tables 15 and 16).

The chlorine obtained in the electrolysis is saturated with water vapours. It is sometimes processed into liquid chlorine. The latter is first cooled after which moisture is condensed from the liquid chlorine. It is then finally dried in towers sprayed with a concentrated sulphuric acid which absorbs moisture contained in the chlorine. The chlorine is converted to a liquid at a compression of not greater than 3 to 6 kgf/cm^2 and cooled to —25 °C.

Liquid chlorine is kept and carried in steel bottles, casks, or tanks with a capacity less than 50 tons.

10.3 Manufacture of Hydrochloric Acid

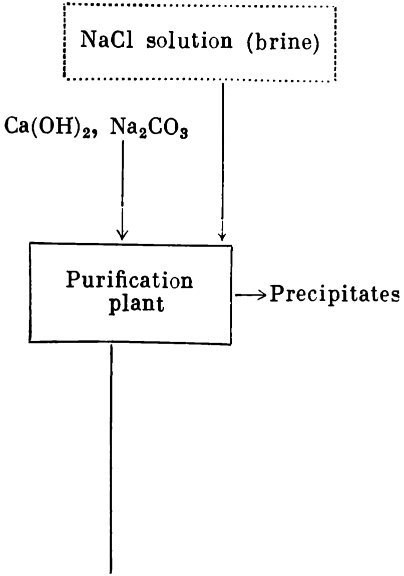
Hydrochloric acid is manufactured in two stages. Hydrogen chloride is first manufactured and then absorbed with water.

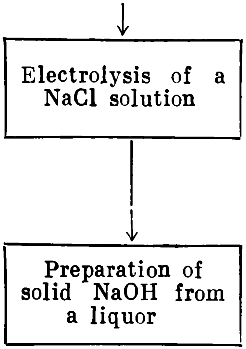
The Manufacture of Hydrogen Chloride. The process can be carried out by three methods: the sulphate method, synthesis from elements, and chlorination of organic compounds.

The sulphate method uses decomposition of common salt with concentrated sulphuric acid (92-93% H_2SO_4) according to this reaction:

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl \qquad (10.13)$$

TABLE 15. **Electrolysis of NaCl Solutions in Baths with Filter (Deposited) Diaphragms**

Process	Operation	Apparatus employed
Preparation of a brine	Cleaning of the brine from calcium and magnesium ions $\left.\begin{matrix} Ca(HCO_3)_2 \\ Mg(HCO_3)_2 \end{matrix}\right\} + nCa(OH)_2 =$ $= \begin{matrix} 2CaCO_3\downarrow + 2H_2O \\ 2CaCO_3\downarrow + Mg(OH)_2\downarrow + 2H_2O \end{matrix}$ $\left.\begin{matrix} CaSO_4 \\ MgCl_2 \end{matrix}\right\} + Na_2CO_3 =$ $= \begin{matrix} CaCO_3\downarrow + Na_2SO_4 \\ MgCO_3\downarrow + 2NaCl \end{matrix}$	 NaCl solution (brine) $Ca(OH)_2$, Na_2CO_3 Purification plant →Precipitates


Electrolysis of a NaCl solution
Preparation of solid NaOH from a liquor

$2H^+ + 2e = H_2$

$2Cl^- - 2e = Cl_2$

$Na^+ + OH^- = NaOH$

Evaporation of the liquor and crystallization of NaCl

Further concentration of the alkali solution

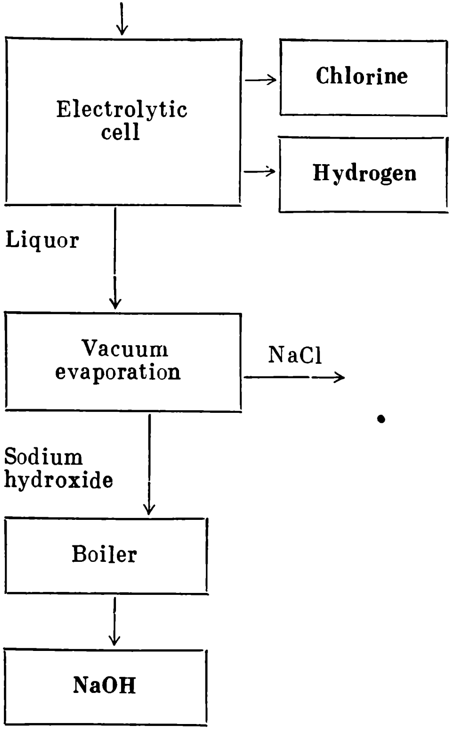
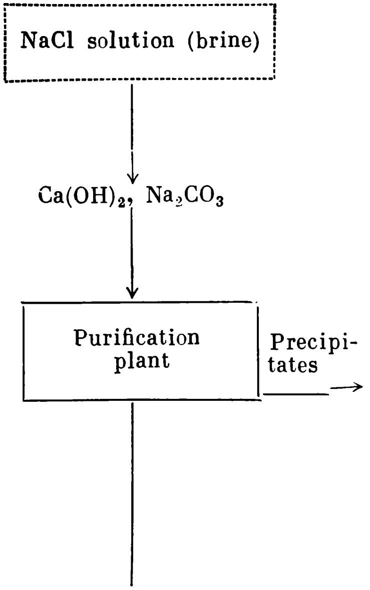
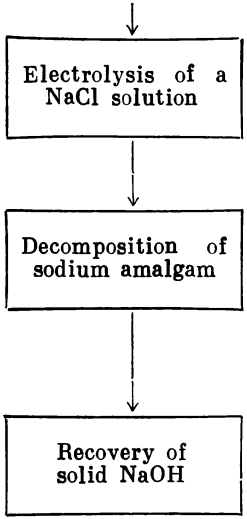


TABLE 16. **Electrolysis of NaCl Solutions in Baths with Mercury-pool Cathodes**

Process	Operation	Apparatus employed
Preparation of a brine	Removal of calcium and magnesium ions from the brine $\left.\begin{matrix} Ca(HCO_3)_2 \\ Mg(HCO_3)_2 \end{matrix}\right\} + Ca(OH)_2 = $ $= \begin{matrix} 2CaCO_3 \downarrow + 2H_2O \\ CaCO_3 \downarrow + Mg(OH)_2 \downarrow + 2H_2O \end{matrix}$ $\left.\begin{matrix} CaSO_4 \\ MgCl_2 \end{matrix}\right\} + Na_2CO_3 =$ $= \begin{matrix} CaCO_3 \downarrow + Na_2SO_4 \\ MgCO_3 \downarrow + 2NaCl \end{matrix}$	 NaCl solution (brine) Ca(OH)₂, Na₂CO₃ Purification plant Precipitates


Electrolysis of a NaCl solution
Decomposition of sodium amalgam
Recovery of solid NaOH

$Na^+ + e = Na$

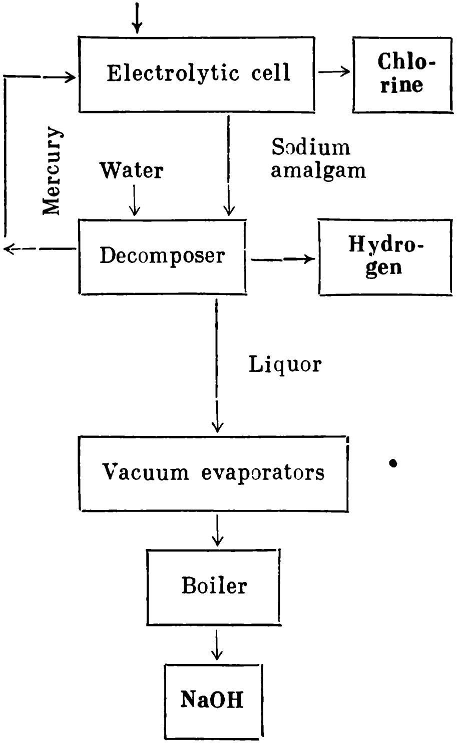
$Na + nHg = NaHg_n$

$2Cl^- - 2e = Cl_2$

$NaHg_n + H_2O = NaOH +$
$+ 0.5H_2 + nHg$

Evaporation of the NaOH solution

Further concentration of the alkali solution



Solid sodium sulphate and gaseous hydrogen chloride are then formed. The reaction is carried out at 500 to 550 °C in muffle furnaces externally heated with hot flue gases.

The gas leaving the furnace contains about 35% HCl. The gas contains impurities, such as arsenic compounds, sulphuric acid vapours, and some other impurities. As hydrogen chloride is absorbed with water, these impurities pass into solution and contaminate the hydrochloric acid, which contains 27-28% HCl.

Thus, a pure acid is difficult to attain by the sulphate method. This process employs sulphuric acid which should preferably be used in the manufacture of products, such as fertilizers. In addition, the process is disadvantageous in that fuel is consumed for heating the reactants. This method may be of interest for manufacture of sodium sulphate. However, because of the discovery of natural sulphate deposits, this method had lost its importance.

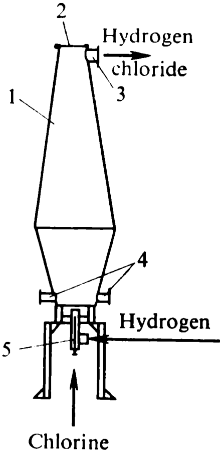


Fig. 71. Furnace for hydrogen chloride synthesis

1—body; *2*—asbestos cover; *3*—branch pipe; *4*—inspection hole; *5*—burner

Hydrogen chloride is synthesized from chlorine and hydrogen, which are produced in the course of electrolysis of a common salt solution, according to the following reaction:

$$Cl_2 + H_2 = 2HCl + Q \tag{10.14}$$

This reaction does not occur under ordinary conditions, or in darkness. When heat is employed with light, the reaction proceeds at a very high rate and an explosion may occur. The temperature rises to about 2300 to 2400 °C because of the heat evolved when chlorine reacts with hydrogen. To utilize chlorine more fully, a 5 to 10 per cent excess of hydrogen is generally used as compared with reaction (10.14).

Hydrogen chloride is synthesized in furnaces (Fig. 71) that are simply constructed. The furnace has steel casing

1. The lower portion of the furnace casing is lined with refractory brick. The furnace bottom accommodates burner *5* which is comprised of two pipes inserted one into the other. Chlorine is fed into the furnace along the inner pipe, and hydrogen, along the outer pipe. The hydrogen chloride is removed from the furnace top through pipe connection *3*. The furnace has inspection holes *4* to watch the combustion of hydrogen in chlorine. The furnace top is closed with asbestos cover *2*, which is forced out by any explosion, thus preventing the furnace from damage.

Synthesizing hydrogen chloride from the elements has some advantages over the sulphate method. These include, first of all, high concentrations (to about 90%) of hydrogen chloride as the gas leaves the furnace and absence of impurities. This yields an acid of greater concentration and higher purity than that produced by the sulphate method, acid is manufactured which contains 31% HCl. The process is also advantageous in that there is no need to consume either sulphuric acid or fuel. Due to these advantages this process has found wide applications.

Chlorination of organic compounds is done to manufacture various chloroderivatives at organic synthesis plants. This process may be illustrated by the reaction of chlorination of benzene:

$$\underset{\text{benzene}}{C_6H_6} + Cl_2 = \underset{\text{chlorobenzene}}{C_6H_5Cl} + HCl \qquad (10.15)$$

The resulting hydrogen chloride is used as a by-product in the manufacture of hydrochloric acid.

Absorption of Hydrogen Chloride with Water. The process evolves heat and the dissolution of hydrogen chloride in water therefore causes the temperature to rise. At the same time, the higher the temperature, the smaller the amount of hydrogen chloride dissolved, since its solubility becomes lower as the temperature rises. Hence, the conclusion can be made that hydrogen chloride absorption should be effected at as low temperatures as possible.

Therefore, formerly, attempts had been made to remove heat from the absorbers to manufacture an acid of higher concentration. To do this, the greatest amount of heat had to be transferred from the absorber to the environment. That was attained by enlarging the heat transfer surface of the absorbers and increasing the number of absorbers that operate in one plant. Here the number of absorbers varied from 30 to 40, thus making the plant more complex and costly.

A. Gasparyan, a Soviet engineer, proved that at very high concentrations of hydrogen chloride in gases, the HCl dissolution heat, if it is not removed to the environment, will be consumed for the evaporation of water from the solution, and the concentration of the resulting acid will become gradually higher. Hence, there is no need to develop the surface of heat transfer to the environment; this makes it possible to reduce considerably the overall dimensions of absorbers. The absorber designed by A. Gasparyan is a packed column. The column is manufactured from acid-proof materials, such as ceramics materials, quartz, plastics (rigid PVC and faolite). The top is sprayed with water, and hydrogen chloride is fed to the bottom. Hydrochloric acid having a concentration of 31 per cent is formed in the column and is removed from the column bottom.

Hydrochloric acid is fed to the users in glass bottles placed in baskets and filled with shavings. Large quantities of hydrochloric acid are carried in special steel tanks, reservoirs and other containers, lined with rubber on the inside.

REVIEW QUESTIONS

1. Name the basic fields of consumption of sodium hydroxide, chlorine, and hydrochloric acid.
2. What are current efficiency and the power utilization factor?
3. What processes occur on the anode and on the cathode in the course of electrolysis of sodium chloride solutions in baths with diaphragms and with mercury-pool cathodes?
4. Name the advantages and disadvantages of electrolytic cells with diaphragms and with mercury-pool cathodes.
5. How is liquid chlorine manufactured?
6. What are the advantages of the process for manufacturing hydrogen chloride by synthesis from chlorine and hydrogen?
7. What is the essence of the method for absorbing hydrogen chloride, as suggested by A. Gasparyan?

Chapter 11

MANUFACTURE OF MINERAL FERTILIZERS AND PESTICIDES

The chemical industry is responsible for realizing this goal. This industry is now becoming a decisive factor in securing high and consistent harvests, and improving the productivity of livestock rearing. Chemistry is being introduced into agriculture on a comprehensive scale involving the application of fertilizers, chemical agents for controlling weeds (herbicides), agents for controlling pests and plant diseases (fungicides), and growth stimulators.

Fertilizers are substances containing elements essential for the nutrition of plants, and are applied to the soil to secure high and consistent harvests. The plants are composed of about 80 chemical elements. The bulk of plants includes carbon, oxygen, and hydrogen. Vital elements are nitrogen, phosphorus, potassium, calcium, magnesium, sulphur, iron, boron, manganese, copper, and zinc.

The atmosphere that surrounds plants and the soil in which they grow are the sources of substances required for the plant nutrition.

Carbon (carbonic acid) and oxygen are assimilated by plants from the air. Small amounts of carbonic acid are assimilated by the root system of plants. Hydrogen is assimilated by plants along with atmospheric precipitation and the moisture in the soil. Nitrogen is assimilated by plants from the soil through the root system in the form of solutions of nitrates, urea, and ammonia. As has been indicated, some nitrogen is assimilated by plants by the fixation processes of atmospheric nitrogen. However, these natural processes do not satisfy the requirement of plants for nitrogen. Therefore nitrogen should be introduced to the soil together with fertilizers. Phosphorus can be assimilated from the soil by plants in the form of soluble phosphates. But these salts are found in small amounts in the soil, and therefore phosphorus is assimilated by plants predominantly from fertilizers applied to the soil. Potassium is also introduced in-

TABLE 17. **An Approximate Increase in the Crop Yield in Applying Hydrogen, Phosphorus, and Potassium into the Soil**

Crop	In tons per ton of applied		
	N	P_2O_5	K_2O
Sugar beet	100	70	40
Potatoes	120	80	60
Raw cotton	12	6	2
Flax fibre	2.5	2	1.5
Winter wheat (grain)	20	25	4

to the soil together with fertilizers. Boron, sulphur, copper, cobalt and some other elements are essential in small amounts for plant development. These elements are called **trace elements**, and the fertilizers that contain them are called **microfertilizers**.

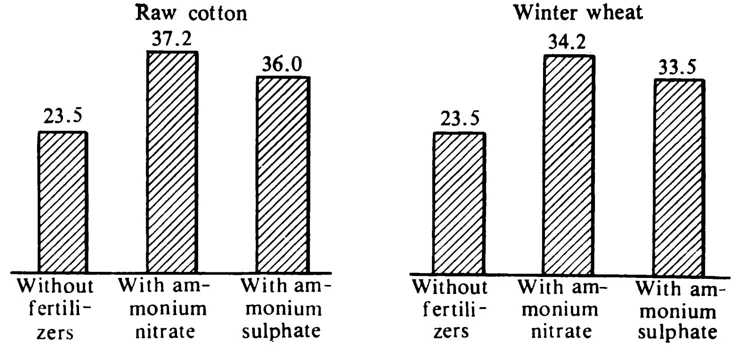


Diagram 11. Crop yields with no fertilizers applied and with nitroge fertilizers (cent/ha)

The amount of chemical elements that can be applied together with fertilizers per hectare of sown area varies in these limits: 30 to 120 kg of nitrogen, 40 to 120 kg of phosphorus (in terms of P_2O_5), 40 to 200 kg of potassium (in terms of K_2O). The results obtained from applying fertilizers are shown in Table 17.

The results of fertilizer utilization are also illustrated in Diagram 11.

Ever growing needs in agriculture for fertilizers were responsible for the further development of this branch of the chemical industry. Taking into account the great variety of soils and climatic conditions in the Soviet Union, the country does not only increase the amount of fertilizers manufactured, but also widens an assortment of fertilizers available. The task is set to manufacture only high-quality fertilizers.

11.1 Classification of Fertilizers

Fertilizers are classified according to their origin, agrochemical purpose, composition, and the number of nutrient elements they contain.

By origin, fertilizers are subdivided into natural and artificial. Natural fertilizers are natural, unprocessed substances like manure, ash from plants, and the so-called agronomical ores (phosphate rocks and apatites). Large amounts of natural fertilizers are used in agriculture, however, they sometimes contain nutrient elements in amounts and in combinations that are not required to improve the yields.

Nutrient elements are assimilated by plants as fertilizers dissolved in soil waters and the resulting solutions are absorbed by the root system of plants.

Thus, fertilizer solubility is the indispensable condition for nutrient elements to be assimilated by plants. Agronomical ores, such as apatite and phosphate rock, contain considerable amounts of phosphorus, but these ores are water insoluble and therefore the phosphorus present in these ores is exceedingly slowly assimilated by plants, i.e. phosphorus is found in an "unassimilable" or "difficultly assimilable" form. Disadvantages inherent to natural fertilizers and the need to increase the amount of fertilizers created the problem of comprehensively developing the synthesis of artificial fertilizers.

Artificial fertilizers manufactured by processing natural materials may have a high content of nutrient elements in their various ratios.

By origin, fertilizers may be subdivided into mineral, organic, organic mineral, and bacterial. **Mineral fertilizers,** manufactured in large amounts at chemical plants, include predominantly inorganic salts, and among organic compounds, carbamide (urea) is used. **Organic fertilizers** contain nutrient elements from the composition of organic compounds. **Mineral organic fertilizers** are a mixture of organic and mineral fertilizers. **Bacterial fertilizers** contain bacterial cultures that promote accumulation of assimilable forms of nutrient elements in the soil.

By agrochemical importance, fertilizers are subdivided into direct and indirect fertilizers. **Direct fertilizers** contain nutrients, such as nitrogen, phosphorus, and potassium, that are assimilated by plants, i.e. direct fertilizers are nutrients for plants. **Indirect fertilizers** are applied to the soil to improve its physical, chemical, and biological properties. Limestone, dolomite, and gypsum are used as indirect fertilizers.

By composition, i.e. by the types of nutrients, direct fertilizers are subdivided into nitrogen, phosphate, potash, and magnesium fertilizers. Microfertilizers are included in a separate group.

By the amount of nutrient elements fertilizers are subdivided into simple and compound fertilizers.

Simple fertilizers contain only one nutrient element, such as nitrogen, phosphorus or potassium. For example, superphosphate contains monocalcium phosphate $Ca(H_2PO_4)_2$, i.e. it contains only one nutrient, phosphorus. This is a simple phosphate fertilizer. Ammonium nitrate contains only nitrogen from among the nutrients and is a simple nitrogen fertilizer. KCl contains potassium, and is a simple potash fertilizer.

Compound fertilizers contain several nutrients in various combinations. For example, ammophos $[NH_4H_2PO_4 + (NH_4)_2HPO_4]$, contains two nutrients, nitrogen and phosphorus, potassium nitrate KNO_3 contains potassium and nitrogen, and a nitrogen phosphorus-potassium fertilizer, which is a mixture of the salts $[NH_4NO_3 + NH_4H_2PO_4 + CaHPO_4 \cdot 2H_2O + KCl + CaSO_4 \cdot 2H_2O]$, is composed of nitrogen, phosphorus, and potassium.

There may be complex and mixed compound fertilizers. **Mixed fertilizers** are manufactured mechanically by mixing simple fertilizers, which include, for example, nitrogen phosphorus-potassium fertilizers. **Complex compound** fertilizers are manufactured using chemical reactions. For example, potassium nitrate is manufactured by reacting nitric acid with potassium chloride.

Fertilizers are also subdivided by the content of the nutrient elements into **concentrated** and **unconcentrated** or **ordinary** fertilizers. The proportion of nitrogen in fertilizers is generally expressed in per cent nitrogen, the proportion of phosphorus in terms of per cent phosphoric anhydride, and the proportion of potassium in terms of per cent potassium oxide. The concentration of nutrients determines in many respects the quality of fertilizers. The higher the concentration of nutrients and the smaller the ballast, the more valuable the fertilizer. The use of concentrated fertilizers makes it possible to reduce the expenses for transporting fertilizers from plants to collective or state farms, for containers and storage of fertilizers, and also for application of fertilizers into the soil. In connection with this, the task is set to increase the industrial manufacture of concentrated fertilizers.

In addition to high nutrient concentration, the quality of fertilizers is determined by their physical properties. Fertilizers should be dry, friable, and suitable for dispersing with mechanical sowers. They must be free from clods or lumps. Fertilizer particles should not be coarse so that plants can more readily assimilate nutrients from these particles. But they should not be too fine, otherwise they will be spread by the wind and turn into dust during transportation or will be too readily dissolved and penetrate into the subsurface layers of the soil. In order to fulfill these conditions granular fertilizers are manufactured as spheres of 2 to 4 mm in diameter.

The index of quality of fertilizers is their ability to absorb moisture, i.e. hygroscopicity. Hygroscopicity of fertilizers determines the conditions of their transportation, storage, and the type of containers.

11.2 Phosphate Fertilizers

The Raw Materials. Phosphorus-containing compounds are to be found in large amounts in nature as phosphate ores, or naturally occurring phosphates, such as apatites and phosphate rocks. The apatite deposits located in Khibiny Mountains on Kola Peninsular are the world's largest. A. Fersman is credited with the discovery of this deposit.

Phosphate rocks and apatites are composed of tricalcium phosphate, $Ca_3(PO_4)_2$, and fluoroapatite, $Ca_5F(PO_4)_3$; these compounds act as sources for preparing phosphorus, which is essential for plants.

The impurities present in phosphate rocks considerably reduce the P_2O_5 concentration in these ores. Some impurities produce an adverse effect on processing ores and on the quality of the fertilizers produced from these ores. Ferric oxide, Fe_2O_3, alumina, Al_2O_3, and carbonic acid salts (carbonates) are especially undesirable impurities. To increase the concentration of calcium phosphates in ores and to reduce the amount of harmful impurities in these ores, naturally occurring phosphates are subjected to beneficiation.

Grinding phosphate rocks produces a phosphate meal. Since $Ca_3(PO_4)_2$ and $Ca_5F(PO_4)_3$ are difficultly soluble in soil waters, the phosphorus contained in the phosphate meal is very slightly and slowly assimilated by plants. Thus, the phosphate meal is a difficultly assimilable fertilizer and, when finely ground, it proves to be effective only on acid podzol soils.

The soluble phosphorus-containing compounds include monocalcium phosphate, $Ca(H_2PO_4)_2$, and dicalcium phosphate, $CaHPO_4$. The monocalcium phosphate is readily soluble in water and is therefore easily assimilated by plants. Fertilizers containing this monocalcium phosphate are called water soluble. The dicalcium phosphate is water insoluble, but soluble in soil acids and is therefore assimilated by plants on acid soils. Whether $CaHPO_4$-containing fertilizers are soluble is judged by whether they are soluble in an ammoniacal solution of ammonium citrate or in a 2% citric acid solution. These fertilizers are called citrate-soluble. Water-soluble and citrate-soluble fertilizers are assimilable phosphate fertilizers.

Artificial phosphate fertilizers are manufactured by converting phosphorus, which is contained in phosphate ores and assimilated with difficulty by plants, into a soluble assimilable form. At the same time, attempts are made to manufacture phosphate fertilizers having the highest phosphorus concentration.

Modern methods for processing phosphate ores into artificial fertilizers may be subdivided into the following groups:

1. Decomposition of naturally occurring phosphates with acids (sulphuric, nitric, phosphoric, and less frequently hydrochloric acids). Water-soluble fertilizers, such as superphosphate and double superphosphate, are predominantly formed.

2. Hydrothermal processing of naturally occurring phosphates, i.e. treatment with steam to form citrate-soluble, fluorine-free phosphates.

3. Decomposition of naturally occurring phosphates by sintering or fusing them at high temperatures with the salts of sodium, potassium, magnesium and alkaline-earth metals to form citrate-soluble fertilizers, such as thermophosphates and fused phosphates. The main phosphate fertilizers that are now being very extensively used include superphosphate and double superphosphate.

The Manufacture of Phosphoric Acid. Phosphoric acid which is essential for the manufacture of some fertilizers, more particularly double superphosphate, is manufactured from phosphate rock or apatites by the wet and dry processes.

The *wet process* is accomplished by using acids to decompose naturally occurring phosphates, normally with sulphuric acid, according to the following reaction:

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O = 2H_3PO_4 + 3(CaSO_4 \cdot 2H_2O) \quad (11.1)$$

The phosphoric acid solution is filtered from the gypsum precipitate. The precipitate is washed with water to remove more fully the phosphoric acid. However, after washing, part of the phosphoric compounds remain in the gypsum, and they are known as **phosphogypsum**.

The setup for manufacturing wet-process phosphoric acid consists of comparatively simple apparatus. The basic apparatus are reactors with agitators and vacuum filters. Wet-process phosphoric acid contains no more than 36 per cent of H_3PO_4. To manufacture double superphosphates and other fertilizers, the wet-process phosphoric acid is, in some cases, evaporated to a concentration of 50 to 75 per cent in drum bubble concentrators. These are only slightly different in their construction and operation from concentrators employed to evaporate sulphuric acid.

The *dry process* for obtaining phosphoric acid consists in reducing the phosphorus contained in naturally occurring phosphates with carbon in the presence of silica in electric furnaces at a temperature of about 1500 °C:

$$Ca_3(PO_4)_2 + 5C + nSiO_2 = P_2 + 3[CaO\cdot nSiO_2] + 5CO \qquad (11.2)$$

The phosphorus obtained is in the vapour state. This process is sometimes called electric sublimation. The oxidation (combustion) of the phosphorus vapours leaving the furnace, or the molten phosphorus, produces phosphoric anhydride:

$$2P_2 + 5O_2 = 2P_2O_5 \qquad (11.3)$$

Then, the phosphoric anhydride reacts with water. Metaphosphoric acid is produced:

$$P_2O_5 + H_2O \rightleftarrows 2HPO_3 \qquad (11.4)$$

which is hydrated (the addition of water) when cooled, and in the presence of excess water to form thermophosphoric acid, H_3PO_4, which is very pure and has a concentration of about 80 to 95 per cent. This acid is suitable for the manufacture of some phosphoric acid salts and the synthesis of organic compounds. When cheap electric power is employed, it is best to use thermophosphoric acid to manufacture concentrated fertilizers (double superphosphate, precipitate, ammophos, etc.).

The Manufacture of Simple Superphosphate. This is a light grey powdery product that includes monocalcium phosphate $Ca(H_2PO_4)_2$.

Naturally occurring phosphates, such as phosphate rocks and apatites, and tower sulphuric acid are used as the raw material to manufacture superphosphate.

This is the reaction that occurs between them:

$$Ca_3(PO_4)_2 + 2H_2SO_4 + nH_2O = Ca(H_2PO_4)_2\cdot H_2O + 2[CaSO_4\cdot 2H_2O] \qquad (11.5)$$

Reaction (11.5) produces a solid mixture of monocalcium phosphate with gypsum, which is called **simple superphosphate** or merely **superphosphate.** Besides, the superphosphate contains compounds of iron, aluminium, silicon or other elements which penetrated into the superphosphate from the raw material.

The reaction of naturally occurring phosphates with sulphuric acid requires a long period of time. The entire process for manufacturing superphosphate is subdivided into a number of stages: (1) grinding of naturally occurring phosphates; (2) mixing the naturally occurring phosphates with sulphuric acid; (3) "maintenance" for some time of superphosphate during which period reaction (11.5) occurs; (4) grinding or "cutting out" of superphosphate; (5) "post-maintenance" of superphosphates at the storage site, i.e. where the interaction of $Ca_3(PO_4)_2$ with sulphuric acid nears completion.

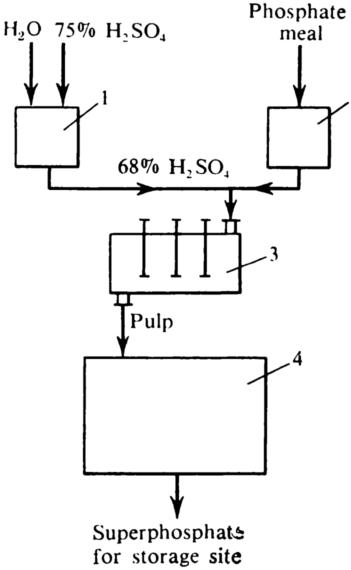


Fig. 72. Diagram for manufacturing simple superphosphate

1—measuring mixer; *2*—scales; *3*—mixer; *4*—ageing chamber

Figure 72 shows the structural diagram for the manufacture of simple superphosphates. A 75% tower sulphuric acid is continuously fed into metering mixer *1* where the acid is diluted with water to a 68% concentration, and then sent to chamber mixer *3*. The phosphate or apatite meal is weighed on automatic balance *2*. The meal is removed from storage to the production process. The phosphate meal is mixed with sulphuric acid in continuous-operation mixer *3*. The pulp obtained from the mixer is sent to continuous-operation "maintenance" chamber *4* where the pulp sets ("solidifies"). After it has been maintained for some time, it is cut out and sent to the storage site.

The continuous-operation mixer (Fig. 73) is made of two or three communicating chambers *4* with high-speed agitators *2* and overflow box *3*. Phosphate rock or apatite and sulphuric acid are fed into the mixer through inlet hole (pipe connection) *1* in the apparatus cover. The residence time of the pulp formed in the mixer is as short as 5 or 6 minutes, and reaction (11.5) between the phosphate rock and the sulphuric acid only begins there. The pulp moves along the entire length of the mixer for a specified period of time and leaves the mixer through overflow box *3* and is fed into a superphosphate chamber.

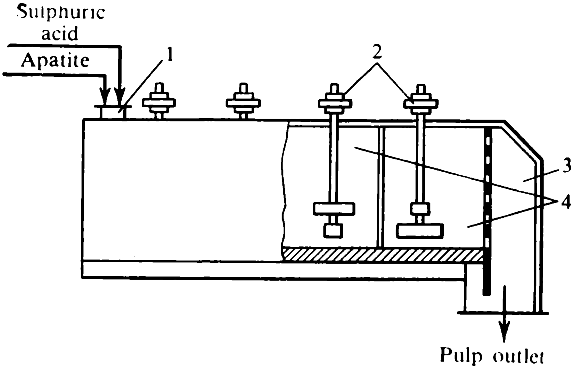


Fig. 73. Continuous-action mixer

1—pipe connection; *2*—mixer; *3*—overflow box; *4*—chambers

The superphosphate chamber where reaction (11.5) occurs is shown in Fig. 74. The reaction of decomposition of the phosphate with sulphuric acid which began in the mixer, continues, the reaction mass sets and solidifies to form a porous superphosphate lump, which is then ground. The reaction between the phosphate and sulphuric acid is very slow, and to make it occur as fully as possible, the reactants should be present in the superphosphate chamber for about 1.5 or 2 hours.

The continuous-operation superphosphate chamber is vertical reinforced concrete cylinder *6* with a steel casing and a concrete bottom. Cylinder *6* revolves slowly (one revolution per 1.5 or 2 hours) around fixed internal cast iron pipe *1*, installed on the foundation and connected firmly with fixed shield *8*. The interior of the chamber accommodates rotary cylinder *3* that is provided with knives, a set of knives for grinding (cutting out) the superphosphate revolves in the opposite direction to the rotation of cylinder *6*. From mixer *5* through the hole in the cover of chamber *4* near fixed shield *8*, the superphosphate pulp

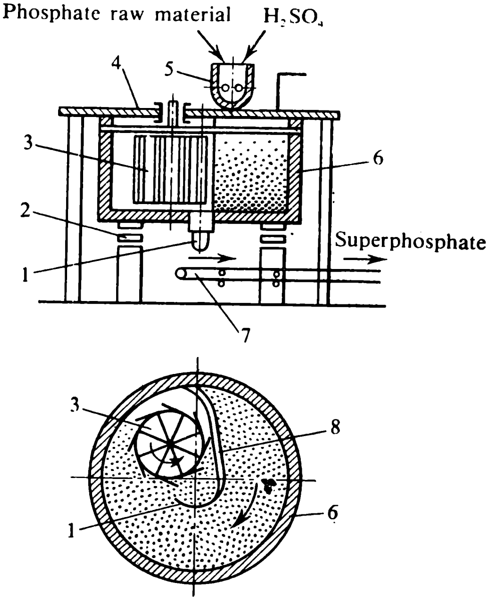


Fig. 74. Continuous-action superphosphate chamber

1—cast iron pipe; *2*—roller bearing; *3*—cylinder fitted with a set of knives; *4*—chamber cover; *5*—mixer; *6*—reinforced concrete cylinder; *7*—conveyer; *8*—fixed shield

is admitted into the annular space between the walls of reinforced concrete cylinder *6* and pipe *1*. The pulp moves together with the revolving body of the chamber. The chamber rotation speed is set so that in one complete revolution, the superphosphate is "maintained", i.e. it solidifies. Once "maintained" at the end of one revolution, the superphosphate is cut out by a set of knives *3*, and falls along central pipe *1* into the conveyer. The conveyer transfers the superphosphate to the storage site. The 7-m dia chamber has a capacity of 50 tons of superphosphate per hour. The storage site is intended not only for storage, but also for production. This is because the reaction between the phosphate and sulphuric acid is not completed in the superphosphate chamber. Six to 20 days are required for the reaction to complete. This process of "post-maintenance" of the superphosphate is completed during the time it is kept in the storage site.

The P_2O_5 content in superphosphate derived from an apatite concentrate is about 20 per cent.

In the manufacture of superphosphate some amount of unreacted acid is retained in it which impairs the quality of the superphosphate. To remove the excess acid, it is neutralized with bone meal or lime to the superphosphate. Sometimes the neutralization is effected with ammonia to obtain ammonated superphosphate containing, in addition to phosphorus, nitrogen.

Ordinary ground superphosphate has the tendency to form lumps or cakes. This makes it difficult for sowers to disperse superphosphate in the field. In addition, when applied into the soil, powdery superphosphate particles are readily soluble in water, and penetrate the subsurface layers of the soil. Therefore, the root system of plants cannot assimilate the greater part of the water-soluble monocalcium phosphate from the fertilizer. These disadvantages of the superphosphate are eliminated when it is granulated. To do this, the superphosphate is wetted with water and passed through an inclined, heated rotary drum. As the drum revolves, the superphosphate is turned into spherical granules to form granular superphosphate.

As has been indicated before, naturally occurring phosphates contain Fe_2O_3 and Al_2O_3. As the phosphates are decomposed with sulphuric acid, these compounds form iron and aluminium sulphates which react with $Ca(H_2PO_4)_2$ and cause phosphorus to penetrate water-insoluble compounds. This process, called **superphosphate retrogradation,** leads to a lower concentration of the assimilable phosphorus in the product. Attempts have been made to use raw material having a low Fe_2O_3 and Al_2O_3 content in the manufacture of superphosphates.

Simple superphosphate is an unconcentrated water-soluble fertilizer. This fertilizer has a low P_2O_5 concentration because decomposing naturally occurring phosphates with sulphuric acid, reaction (11.5), yields gypsum, $CaSO_4 \cdot 2H_2O$, in addition to monocalcium phosphate. This is the ballast reducing the P_2O_5 concentration in the product. Hence, to increase the P_2O_5 concentration in the superphosphate, an acid should be chosen so that only monocalcium phosphate, $Ca(H_2PO_4)_2$, not other calcium salts will be formed when the naturally occurring phosphates are decomposed by the acid.

The Manufacture of Double Superphosphate. To manufacture double superphosphate, which contains only $Ca(H_2PO_4)_2$ (in addition to impurities that penetrated superphosphate from the raw material), naturally occurring phosphates are decomposed with phosphoric acid:

$$Ca_3(PO_4)_2 + 4H_3PO_4 + nH_2O = 3[Ca(H_2PO_4)_2 \cdot H_2O] \qquad (11.6)$$

Double superphosphate is a concentrated fertilizer containing 42 to 48 per cent of P_2O_5.

The technological processes to manufacture double superphosphate and simple superphosphate are identical. As with simple superphosphate, double superphosphates are subjected to granulation and ammoniation.

The decomposition processes in the raw material phosphate such as apatites, $Ca_5F(PO_4)_3$, with acids (the manufacture of phosphoric acid, simple and double superphosphates) evolve gases that contain fluorine compounds, like HF and SiF_4. They are treated with water to form silicofluoric acid H_2SiF_6, which is then turned into Na_2SiF_6, NaF, and $(NH_4)_2SiF_6$.

The Manufacture of Precipitate $CaHPO_4 \cdot 2H_2O$. This process consists of neutralizing phosphoric acid with limestone and then with lime milk:

$$3H_3PO_4 + 2CaCO_3 = CaHPO_4 \cdot 2H_2O + Ca(H_2PO_4)_2 + 2CO_2 \qquad (11.7)$$

$$Ca(H_2PO_4)_2 + Ca(OH)_2 = 2CaHPO_4 \cdot 2H_2O \qquad (11.8)$$

The resulting precipitate is filtered from the solution and dried. This fertilizer contains 42 per cent of P_2O_5 in a citrate-soluble form. The comparatively high cost of a unit of P_2O_5 in the precipitate limits its production.

The Manufacture of Thermophosphates and Fused Phosphates. Naturally occurring phosphates are converted to a state assimilable by plants by sintering with alkalis at 1200 °C to form so-called **thermophosphates**. Phosphates are fused with silicates to form **fused phosphates**. Thermophosphates and fused phosphates contain 20 to 30 per cent of P_2O_5 in a citrate-soluble form assimilable by plants, and are applied into acid soils.

A fertilizer which is identical in composition to fused phosphates is Thomas slag. It is derived from making steel from iron with a higher phosphorus content. Thomas slag does not contain more than 20 per cent of P_2O_5 in a citrate-soluble form.

11.3 Nitrogen Fertilizers

Nitrogen fertilizers are synthesized from nitric or sulphuric acid, ammonia, carbon dioxide, and calcium hydroxide. All nitrogen fertilizers are readily soluble in water and assimilable by plants.

Nitrogen fertilizers are subdivided into ammonia, nitrate, ammonia-nitrate, and amide fertilizers. Ammonia fertilizers contain nitrogen in NH_4^+ cation form (ammonium sulphate, $(NH_4)_2SO_4$), nitrate fertilizers, in NO_3^- anion form (calcium nitrate, $Ca(NO_3)_2$, or sodium nitrate, $NaNO_3$), ammonia-nitrate fertilizers, in NH_4^+ cation and NO_3^- anion forms (ammonium nitrate, NH_4NO_3), amide fertilizers, in NH_2 group form (carbamide, $CO(NH_2)_2$).

The following nitrogen fertilizers are manufactured industrially: ammonium nitrate, carbamide, ammonium sulphate, and sodium nitrate.

The Manufacture of Ammonium Nitrate. Ammonium nitrate is a concentrated nitrogen fertilizer containing about 35 per cent of N. This is the most available nitrogen fertilizer in the Soviet Union and is usable on practically any soils or any crops. In addition to agriculture, ammonium nitrate is used to manufacture explosives.

In addition to its advantages, ammonium nitrate has substantial disadvantages as a fertilizer. When stored or transported, it disperses into the air or forms cakes and large aggregates. As a result, instead of a product readily appliable to the soil, large lumps or blocks of ammonium nitrate are formed. They must be specially ground. Ammonium nitrate is explosive and is a fire hazard. This makes it more difficult to manufacture and apply.

In compliance with GOST 2-65, the Soviet Union produces two grades of ammonium nitrate: grade A is a crystalline or lamella form containing at least 34.8 per cent of N and not more than 0.5 per cent of H_2O; grade B is manufactured in granular form containing 34.2 per cent of N and with a maximum humidity content of 0.4 per cent.

Ammonium nitrate is derived from ammonia and nitric acid according to the following reaction:

$$NH_3 + HNO_3 = NH_4NO_3 \tag{11.9}$$

This reaction proceeds with intense heat evolution.

To manufacture ammonium nitrate, synthetic ammonia and an unconcentrated (50-55%) nitric acid are generally used. The neutralization of an unconcentrated nitric acid with ammonia produces a solution containing about 50 per cent of ammonium nitrate. Due to the heat evolved during the neutralization reaction, water evaporates from this solution to form a more concentrated, 80%, ammonium nitrate solution. Using neutralization heat to manufacture ammonium nitrate presents certain difficulties. To utilize this heat, special apparatus, such as neutralizers (apparatus utilizing neutralization heat) are installed.

A neutralizer utilizing neutralization heat (Fig. 75) is a cylindrically shaped stainless steel vessel *1*. Its interior accommodates a second vessel *2*. Nitric acid and ammonia are continuously fed into cylinder *2*, and the neutralization reaction occurs in this vessel (11.9). The ammonium nitrate solution produced in cylinder *2* is fed into annular space *3* between the external and internal cylinders of the neutralizer. The heat evolved in cylinder *2* during neutralization is transferred to the solution in the annular space through the cylinder walls. This solution is then evaporated. The water vapours are removed from the top of annular space *3*. The evaporated ammonium nitrate solution is removed from the apparatus through tubes *4*, and a fresh amount of ammonia is added to the solution to complete neutralization. The solution is then evaporated to obtain a fusion cake of ammonium nitrate containing 98-99 per cent of NH_4NO_3. Cooling the fusion cake may produce ammonium nitrate crystals.

Ammonium nitrate is "powdered" with finely divided limestone, phosphate rock meal, gypsum, and kaolin to reduce its caking tendency. These additives form laminations, as it were, between the crystals of ammonium nitrate and prevent them from being stuck together.

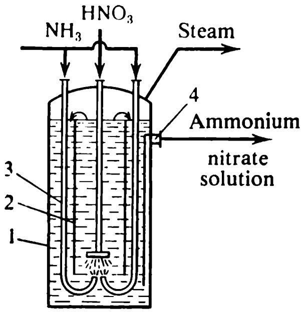


Fig. 75. Apparatus utilizing neutralization heat

1—apparatus body; *2*—inner cylinder; *3*—annular space; *4*—pipe

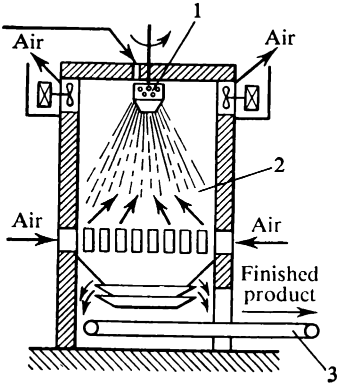


Fig. 76. Cranulation tower

1—rotary basket; *2*—granulation tower; 3—conveyer

The most effective method for improving the properties of ammonium nitrate is to granulate it. This produces ammonium nitrate as spheres 2 or 3 mm in diameter. Ammonium nitrate is granulated in hollow reinforced concrete granulation towers 30 to 35 m high (Fig. 76). Perforated rotary basket *1* is located at the top of the tower, and a hot fused cake of ammonium nitrate is fed into the basket. As the basket revolves, the fused cake is scattered through holes in the basket, and from the bottom cold air moves in countercurrent to the fused cake. When it comes into contact with the cold air, drops of the falling fused cake solidify and fall in the form of granules onto conveyer *3* which transfers the product for drying and packing purposes.

The Manufacture of Carbamide (Urea). Carbamide, or urea, $(NH_2)_2CO$, is the most valuable nitrogen fertilizer. It contains about 46 per cent of N and carbon which is readily assimilable by plants. Urea is also more effective than ammonium nitrate, since applying nitrogen as urea to the soil increases the crop yield to a greater extent than applying the same amount of nitrogen as ammonium nitrate. Carbamide is not only a fertilizer, it has also found application in livestock rearing as fodder additive.

In addition to agricultural applications, carbamide is widely used to manufacture plastics. It is employed to manufacture urea-formaldehyde or carbamide resins, and also varnishes possessing strength, thermal resistance, and light fastness. Carbamide is also employed to manufacture moisture-resistant adhesives. The pharmaceutical industry produces carbamide-based sedatives and soporifics.

Carbamide is derived from liquid ammonia and carbon dioxide. The process for producing carbamide is rather complicated. The reaction:

$$2NH_3 + CO_2 = (NH_2)_2CO + H_2O \tag{11.10}$$

only occurs at a pressure of about 200 kgf/cm^2 and a temperature of about 200 °C. This synthesis occurs in a thick-walled column.

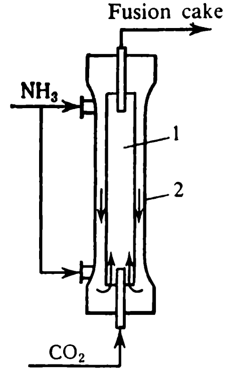


Fig. 77. Urea synthesis column

1—inner cylinder; *2*—column

The schematic diagram of an urea synthesis column is shown in Fig. 77. The interior of column *2* accommodates cylinder *1*. Liquid ammonia is fed by a pump into the annular space between the body and the internal cylinder. It is then admitted into cylinder *1*. Carbon dioxide is admitted at the bottom of cylinder *1*. Ammonia and carbon dioxide react with each other to form a fused cake which contains carbamide, other products derived from ammonia and carbon dioxide, and also the unreacted ammonia and carbon dioxide. The fused cake is removed from the top of the column, and carbamide is then derived from the fused cake. Carbamide is sent to users either in crystalline or granular form, as is ammonium nitrate.

Ammonium sulphate is a white crystalline product. It is prepared by neutralizing sulphuric acid with gaseous ammonia:

$$H_2SO_4 + 2NH_3 = (NH_4)_2SO_4 \qquad (11.11)$$

To manufacture ammonium sulphate, tower sulphuric acid and ammonia contained in a coke-oven gas resulting from coal coking are used.

Ammonium sulphate is an unconcentrated nitrogen fertilizer containing as little as 20-21 per cent of N. In addition, ammonium nitrate is disadvantageous in that when the fertilizer is applied to the soil, the SO_4^{2-} ion present in the fertilizer acidifies the soil. However, ammonium sulphate is advantageous over other fertilizers for it neither cakes during storage, nor is impregnated with moisture, nor it is fire hazard.

Sodium Nitrate or Chile Saltpeter. Sodium nitrate is an unconcentrated fertilizer having a nitrogen content of about 16 per cent. Sodium nitrate is produced from a solution of soda or sodium hydroxide and nitric oxides found in the waste gases of nitrate setups. This fertilizer is manufactured from nitric acid waste products and therefore, despite the low nitrogen concentration in the fertilizer, it is desirable to manufacture it. In this way, two problems are simultaneously solved: firstly, fertilizers are manufactured and, secondly, the gases released into the atmosphere are rendering harmless at integrated nitrogen-mineral fertilizer plants.

Liquid Nitrogen Fertilizers. Liquid nitrogen fertilizers are either aqueous ammonia solutions (ammonia water), or solutions that contain ammonium nitrate or urea in addition to ammonia. These concentrated nitrogen fertilizers are applied to the soil by special machines like those used for watering streets. Use of liquid fertilizers in the fields showed them to be highly effective. For example, when 200 kg of ammonia water were applied per hectare, the average crop growth was 6.4 cent for spring wheat, 152 cent for maise, and 27 cent for sugar beet.

11.4 Potash Fertilizers

Potash, as well as nitrogen and phosphate fertilizers, has great importance for the intensification of agriculture.

Plant ash containing potassium carbonate K_2CO_3 has long been used as potash fertilizers. This source of potassium could not meet the needs of agriculture in potassium. Therefore, manufacture of potash fertilizers began in the middle of the 19th century when potassium salt deposits were discovered. Commercial potassium chloride was first manufactured in 1861. Since then the manufacture of potassium salts became a major branch of the chemical industry. At the present time, about 90 per cent of the potassium salts mined are used as potash fertilizers, the remainder being used to manufacture other chemical products.

In natural conditions potassium is incorporated in several minerals. The Soviet Union has the largest deposits of sylvinite and carnallite.

Sylvinite is a mixture containing about 30 per cent of potassium chloride and 70 per cent of sodium chloride. *Carnallite*, $KCl \cdot MgCl_2 \cdot 6H_2O$, contains magnesium chloride, in addition to potassium chloride. Naturally occurring potassium salts (primarily ground sylvinite) and their products are used as fertilizers. Naturally occurring potassium salts (the raw material) contain from 15 to 22 per cent of potassium in terms of K_2O. To manufacture potash fertilizers, it is essential to recover potassium chloride from the minerals that contain it.

Processing of Sylvinite. This process separates the potassium chloride and sodium chloride contained in sylvinite. One of the methods for producing potassium chloride from sylvinite is based on the fact that the solubility of potassium chloride in hot water is higher than in cold water; the higher the water temperature, the more potassium chloride may be dissolved in water. The solubility of sodium chloride changes very slightly as the temperature rises. Therefore, about the same amount of common salt is soluble in hot and cold water. Hence, if ground sylvinite is dissolved in hot water both potassium chloride and sodium chloride will pass into solution. Cooling this solution saturated with two salts at high temperatures causes only potassium chloride to crystallize, since at lower temperatures the solubility of potassium chloride is lower. The sodium chloride, whose solubility is almost independent of temperature, remains in solution. The potassium chloride crystals are separated from the solution. The solution resulting from the separation of KCl crystals (the mother liquor) is used for dissolving fresh portions of sylvinite.

In practice, ground sylvinite is treated at a temperature of about 100 °C with a mother liquor containing sodium chloride and a small amount of potassium chloride, rather than with water (Diagram 12). Since the solution is saturated with sodium chloride, the potassium chloride passes into solution from the sylvinite and the sodium chloride almost does not dissolve. A hot solution of potassium chloride is separated by filtering the undissolved sodium chloride and then cooled to 20 or 30 °C. Cooling the solution causes the potassium chloride to crystallize, the sodium chloride remaining in solution. The potassium chloride crystals are separated from the solution, dried and packed.

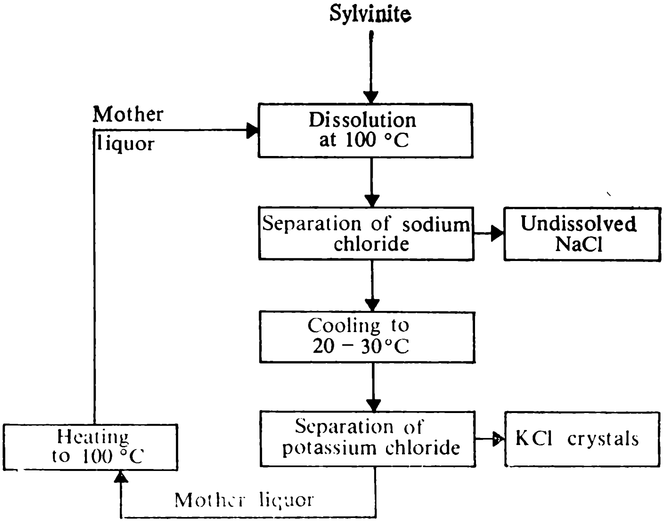


Diagram 12. Sylvinite processing

The mother liquor, resulting from the separation of the potassium chloride, is heated and again used to treat sylvinite.

A method for recovering potassium chloride from sylvinite, i.e. **flotation**, has been developed. Flotation of sylvinite is effected in a solution saturated with potassium chloride and sodium chloride. The potassium chloride, whose wettability is lower than that of the sodium chloride, is removed together with the froth, the sodium chloride falling onto the bottom of the apparatus. The separation of sylvinite by this method yields industrial potassium chloride.

Industrial potassium chloride has limited application as a fertilizer. It is used to manufacture compound fertilizers, more particularly, it acts as the starting product for manufacture of potassium nitrate, potassium-ammonium nitrate, nitrogen-phosphorus-potassium fertilizers, and other fertilizers.

11.5 Compound Fertilizers

Compound fertilizers may be complex or mixed. They are generally manufactured in granular form. They are concentrated fertilizers, since they simultaneously contain several nutrient elements (a total of 50 to 70 per cent of N, P_2O_5 and K_2O). In addition to nitrogen, phosphorus, and potassium, these fertilizers may contain trace elements. Owing to the valuable properties of compound fertilizers, their agricultural application helps to cut down substantially labour expenditures. For example, the saving in applying the compound fertilizers to the soil, as compared with the labour expenditures for applying the same amount of simple fertilizers, is 0.3 man-h per hectare. The saving that resulted from simultaneously applying several nutrient elements into the soil, and the increase in their concentration in fertilizers promoted manufacture of compound fertilizers on an increasing scale. The manufacture of these fertilizers was, for the first time, begun in the Soviet Union in the thirties. At the present time, the Soviet Union makes a great number of grades of compound fertilizers that differ in composition and the ratio of their nutrient elements.

To abbreviate the composition of fertilizers, the content of nutrient elements in this composition is designated by numerals separated from each other by dash symbols. The first numeral indicates the percentage of nitrogen, the second numeral—phosphoric anhydride, and the third numeral—potassium oxide. For example, if the compound fertilizer contains 10% N, 15% P_2O_5, and 10% K_2O, it will be designated as 10-15-10. If the fertilizer contains only 10% N and 15% P_2O_5, it is designated as 10-15-0.

The Manufacture of Complex Fertilizers. *Ammophos* contains two nutrient elements, nitrogen and phosphorus. It predominantly consists of monoammonium phosphate $NH_4H_2PO_4$ (80 to 90%) and diammonium phosphate $(NH_4)_2HPO_4$ (10 to 20%). Ammophos is a concentrated fertilizer containing about 10 to 13 per cent of N and 47 to 50 per cent of P_2O_5 in water-soluble form.

Ammophos is obtained by neutralizing phosphoric acid, most frequently wet-process phosphoric acid, with ammonia according to the following reactions:

$$H_3PO_4 + NH_3 = NH_4H_2PO_4 \tag{11.12}$$

$$NH_4H_2PO_4 + NH_3 = (NH_4)_2HPO_4 \tag{11.13}$$

Setups manufacturing granular ammophos employ unevaporated phosphoric acid having about 25 per cent of P_2O_5. The phosphoric acid is neutralized with ammonia in consecutively arranged reactors. The pulp temperature does not exceed 90 °C, and ammonia losses are small. The pulp is dried with flue gases in a spray drier. The dried powdery product is granulated, slightly dried, and graded.

The *nitrogen-phosphorus-potassium fertilizer* is a fertilizer containing three nutrient elements, i.e. phosphorus, nitrogen, and potassium, in the form of dicalcium phosphate $CaHPO_4$, ammonium nitrate, ammonium phosphates, and potassium salts. Nitrogen-phosphorus-potassium fertilizer contains 12 to 20% N, 10 to 14% P_2O_5, and 10 to 21% K_2O in citrate-soluble and water-soluble forms.

Nitrogen-phosphorus-potassium fertilizer is derived from the products of decomposition of naturally occurring phosphates with 47-55% nitric acid:

$$Ca_3(PO_4)_2 + 6HNO_3 = 2H_3PO_4 + 3Ca(NO_3)_2 \tag{11.14}$$

The solution (extract) resulting from decomposition contains phosphoric acid and calcium nitrate which, when processed, remains in the fertilizer and greatly impairs the quality of the product. Hence, $Ca(NO_3)_2$ should be removed from the solution. Freezing is one of the methods used to remove calcium nitrate from the solution. To do this, the solution is cooled to temperatures of —5 °C or —10 °C. Cooling crystallizes $Ca(NO_3)_2 \cdot 4H_2O$ and the crystals are then separated from the solution. The mother liquor containing basically phosphoric acid and dissolved $Ca(NO_3)_2$ is ammoniated. The ammoniation process occurs according to the following reaction:

$$Ca(NO_3)_2 + 2H_3PO_4 + 3NH_3 + H_2O = CaHPO_4 + NH_4H_2PO_4 + 2NH_4NO_3 \quad (11.15)$$

The pulp is then evaporated, and KCl is added to the pulp and granulated.

The Manufacture of Mixed Fertilizers. The process consists of mixing simple fertilizers, or simple and compound fertilizers. $NaNO_3$, $(NH_4)_2SO_4$, urea, ammoniated superphosphate, and NH_4NO_3 are used to obtain mixtures. To make high-quality mixed fertilizers, the components to be introduced into the mixture should be dry, have an identical density, and an approximately similar particle size. When mixing the components, there should be no chemical reactions that could lose nutrient elements. When compared with compound fertilizers, the ratios of the nutrient elements may be considerably more varied in mixed fertilizers.

11.6 Microfertilizers

Along with ordinary nitrogen, phosphate, and potash fertilizers, **microfertilizers** are very important for increasing crop capacity and improving the quality of farm products. Microfertilizers contain boron, copper, manganese, zinc, molybdenum, and some other elements (trace elements) required by plants in minor amounts. There are some soils where plants cannot grow without microfertilizers; plants "become ill", resulting in a poor crop yield.

When trace elements are in short supply in the soil, crop yield does not only become poorer, but the farm products will have an inadequate amount of trace elements. Using these products to feed humans and animals may provoke diseases.

Microfertilizers are applied to the soil in very minor amounts. 0.5-1.5 kg per hectare is sufficient to increase the yield and improve the quality of the crop.

Boron fertilizers including boric acid H_3BO_3, borax $Na_2B_4O_7$, magnesium borate $Mg(BO_3)_2$, and boric superphosphate can be used as microfertilizers.

Copper fertilizers are applied to the soil in solid form and in the form of copper salt solutions. Copper fertilizers include copper vitriol $CuSO_4$. This is a highly effective, but still expensive fertilizer. Instead, the wastes from sulphuric acid production, such as pyrite cinder, low-grade copper ores, and others may be used.

Manganese fertilizers are predominantly manganese slimes, which are manganese ore processing waste.

Zinc fertilizers are sulphates and other zinc salts.

Molybdenum fertilizers are ammonium and sodium molybdates, $(NH_4)_2MoO_4$ and Na_2MoO_4, superphosphate that contains molybdenum (molybdenum-containing superphosphate), and molybdenum trioxide MoO_3.

11.7 Pesticides

Chemically protecting plants from pests, diseases, and weeds is exceptionally important. In some countries losses caused by pests and plant diseases are between 10 to 80 per cent of the crop yield. Weeding plants is hard work to do.

Using **pesticides** to fight pests, diseases, and undesirable plants is highly effective. The application of pesticides is of immense importance for the national economy; it increases the crop capacity, preserves the reserves, and increases the labour productivity in agriculture. Pesticides are organic and inorganic substances that include compounds of arsenic, fluorine, chlorine, sulphur, phosphorus, mercury, and copper, Pesticides should be as toxic as possible to insects and fungous organisms, but as harmless as possible to humans and animals. Pesticides are subdivided according to application: insecticides, chemicals for fighting insects; fungicides, chemicals for fighting fungous diseases in plants; herbicides, chemicals for killing weeds and undesirable vegetation; defoliants, chemicals for removing leaves of cotton plants, sugar beet, and other crops before they are harvested by machines.

Insecticides act within insects, or affect them when on their body surface or when they are impregnated into the juices of plants and render them toxic to insects. Insecticides are applied as powders (dusts) for dusting, as solutions for spraying, or as fumes for the fumigation of plants by machines or aircraft.

Insecticides include arsenic compounds, such as $NaAsO_2$, $Ca(AsO_2)_2$, $Ca_3(AsO_4)_2$, Na_3AsO_4, $Cu(CH_3COO)_2 \cdot 3Cu(AsO_2)_2$; compounds that include chlorine, such as dichlorodiphenyltrichloroethane $CCl_3CH(C_6H_4Cl)_2$, hexachlorane $C_6H_6Cl_6$; and phosphorus compounds, such as thiophos $(C_2H_5O)_2PSOC_6H_4NO_2$.

Fungicides are used to spray, dust, and fumigate plants and seeds. The most widely used fungicides are copper vitriol, ground sulphur, Bordeaux liquid (a mixture of a copper vitriol solution and lime milk), mercury-chloride sublimate $HgCl_2$, ceresan, or a NIUIF-2 compound containing ethylmercuric chloride, C_2H_5HgCl.

Herbicides can be used to kill the whole vegetation when preparing land for ploughing (non-selective herbicides) or when weeding (selective herbicides). Solutions of copper vitriol, of iron vitriol $FeSO_4$, powders of calcium cyanamide $CaCN_2$, and derivatives of phenoxyacetic acid, $C_6H_5OCH_2COOH$, have found application as herbicides.

Defoliants are calcium cyanamide and sodium pentachlorophenolate C_6Cl_5ONa.

In addition to these pesticides **compounds for seed treatment** are used for their disinfection. **Antiseptics** are agents for preventing the products of vegetable and animal origin from being damaged by microorganisms. **Rodent poisons** are agents used to kill rodents and other undesirable animals.

REVIEW QUESTIONS

1. What elements are of the greatest importance for plant activity?
2. What elements make deplete the soil when increasing the crop yield?
3. What are mineral fertilizers and how are they classified?
4. What advantages do concentrated and compound fertilizers have?
5. Name the most significant deposits of naturally occurring minerals containing phosphorus and potassium compounds.
6. What processes for manufacturing phosphoric acid do you know?
7. What is the purpose of treating phosphate rock and apatite with sulphuric or phosphoric acid? What are simple and double superphosphates?
8. Draw the diagram for the operation of the superphosphate chamber.
9. What are thermophosphates, fused phosphates, and Thomas slag?
10. What properties of ammonium nitrate make its storage and application difficult as a fertilizer?
11. Why is the neutralizer used to manufacture ammonium nitrate called an apparatus utilizing the neutralization heat?
12. What are the agricultural and industrial applications of carbamide (urea)? Write the reaction for its manufacture.
13. How is sylvinite processed?
14. What compound fertilizers do you know?
15. What elements are applied to the soil together with microfertilizers?
16. Classify pesticides.

Chapter 12

CHEMICAL PROCESSING OF SOLID FUELS

The concept "fuel" is associated in our mind with combustion. Yet, fuel is not only the source for producing heat, but also acts as a raw material in the chemical industry. Rubbers and fabrics, airplane components and consumer goods, fertilizers and dyes are all manufactured from this raw material. Fuels are referred to as naturally occurring or artificially manufactured compounds that are a source of heat energy and a raw material for the chemical industry. The world's fuel reserves are immense. For example, according to the data obtained by A. Fersman, brown coal accounts for 2100 billion tons, black coal for 3200 billion tons, and anthracite for 600 billion tons. The world's annual production of all types of coal constitutes more than a billion tons. In addition to coal, the Earth contains combustible shales, petroleum, and gases.

Processing vegetable fuel, like wood, has great importance.

All types of fuel are used as raw materials for the chemical industry.

12.1 Classification of Fuels

All fuels can be subdivided by the state of aggregation into solid, liquid, and gaseous fuels, and **by origin**, natural and artificial fuels.

Naturally occurring fuels include solid fuels, such as coals, wood, shales and peat; liquid fuels—petroleum; gaseous fuels, such as natural and casing-head gases.

Artificial fuels result from processing naturally occurring fuels. *Solid* artificial fuels include coke, semicoke, and charcoal; *liquid* fuels include gasoline, kerosene, and ligroin; *gaseous* fuels include producer gases, coke-oven gas, and refinery gases.

There is much common in the chemical methods of their processing despite various types of fuels. In most cases fuel processing is conducted at very high temperatures.

Processes occurring at high temperatures are called pyrogenic (the Greek word "pyro" means fire, and "genos", birth).

Some fuels are processed at low temperatures. Here, fuels are treated with acids, alkalis or some other reactants. This method has found especially wide application in processing wood to manufacture cellulose, ethanol, and other products. Despite the fact that the methods of fuel processing are identical, the amount and the composition of these products are different.

This chapter deals with the methods of solid fuel processing.

12.2 The Composition of Solid Fuels

Solid fossil fuels originated from plants that formerly covered the Earth's surface. The process of converting plants to fossil combustibles occurred over millions of years. Peat was formed from plants, which as time went by became brown coal, which became black coal. As coal formed, the composition of the fuel underwent changes, the content of carbon became higher and of hydrogen and oxygen lower. Anthracite and black coal—"old" fuels—have the highest carbon content. Wood and peat—"young" fuels, have the lowest carbon content.

TABLE 18. **The Composition of Organic Mass in Fuels (per cent)**

Type of fuel	Carbon	Hydrogen	Oxygen and nitrogen
Wood	44	6	50
Peat	59	6	35
Brown coal	70	5.5	24.5
Black coal	82	5	13
Anthracite	95	2	3

Table 18 shows the composition of *organic* or *combustible part* of fuels, i.e. the portion of fuel that gives off heat during the combustion process. The elements incorporated into the organic mass of fuels are bonded together to form organic compounds. Besides, a fuel contains an *incombustible part* or *ballast* which gives no heat during the combustion of a fuel. The incombustible part of a fuel is composed of moisture and ash; the ash content in a fuel varies from 2 to 30 per cent in coals, and the moisture content, from 1 to 50 per cent. The lower the ash content and the moisture content of a fuel, the higher its quality.

Coals are one of the basic types of fuel and are a source for producing a synthetic fuel and a chemical raw material. These are the basic methods for coal processing: coking, low-temperature carbonization, and gasification.

12.3 Coal Coking

Coal coking is done by heating coal in the absence of air at temperatures of 900 to 1100 °C. The coking products are solid product—coke; liquid products—coal tar, crude benzene, and tar water; and a gaseous product—coke-oven gas.

Coke is a dull black, porous solid material. It is used primarily in the iron and steel industry. It is also employed for gasification purposes, to manufacture calcium carbide and other products.

Coal tar is a black, viscous, heavier than water product having a specific odour and containing about 300 various compounds. Benzene, toluene, xylenes, phenol, cresols, pyridine, naphthalene, anthracene, and other compounds that are essential in the manufacture of plastics and chemical fibres are derived from coal tar.

Crude benzene is a mixture that results from coking. It contains carbon disulphide, benzene, toluene, xylenes, and other compounds.

Tar water is a weak aqueous solution of ammonia and ammonium salts. Ammonia may be recovered from tar water and used to manufacture fertilizers.

Coke-oven gas is a mixture containing hydrogen, methane, ethylene, carbon monoxide, nitrogen, and other compounds. The combustion of coke-oven gas may produce heat. However, the compounds contained in this gas may act as a raw material for chemical fibres and therefore it is not rational to use coke-oven gas as the heat source.

Coking is one of the oldest chemical industries, it has existed for more than 200 years. This process came into being in Britain in 1735 because of the need to find a replacement for charcoal in the blast-furnace process in cast iron making. Up to the middle of the 19th century, coking was done for the sole purpose of producing coke for the iron and steel industry. Vapours of coal tar and crude benzene, coke-oven gas, and ammonia were discharged into the atmosphere or burned in ovens.

In the second part of the 19th century the situation had drastically changed. The synthesis of nitrobenzene from benzene by Mitcherlikh and deriving aniline from nitrobenzene by V. Zinin in Russia, was the turning point. These discoveries laid the foundation for creating the aniline and paint industry, and subsequently the pharmaceutical and explosive-making industries. Benzene, toluene, phenols, cresols, naphthalene, anthracene, and other products contained in coal tar and in crude benzene were required for these industries. Since that time coal tar and crude benzene were turned from industrial waste products into basic and major products. The construction of installations for entrapping coal tar and crude benzene began almost in every plant. Thus, integral by-product coke industries were created. In addition to coke, benzene, xylene, naphthalene, anthracene, phenols, and other products were manufactured.

The Raw Materials. The raw materials for coking include coking coals (grade C) which can be readily sintered at high temperatures to give strong and porous coke. However, a mixture, that is a charge, is made under industrial conditions. It also includes coals of other grades. Blending makes it possible to expand the raw material base of the by-product coke industry, and, in addition to high-quality coke, produce large amounts of coal tar, crude benzene, and coke-oven gas.

One ton of dry coal gives an average of 700 to 800 kg of coke, 25 to 50 kg of coal tar, and 300 to 350 m^3 of a gas containing about 3 kg of ammonia and about 10 kg of crude benzene.

Coking. To carry out this process, coke-oven batteries are used which are made of a number of chambers where coal is heated to about 900 to 1100 °C in the absence of air. In these conditions coal gives off vapours of coal tar, crude benzene, water, and coke-oven gas. The vaporous and gaseous products are continuously removed from the oven and by the end of the coking period, which lasts 14 or 15 hours, the oven contains coke in the form of a porous and sintered "cake". Since the process is carried out at very high temperatures, the chamber walls are lined with materials that can withstand high temperature. Such materials are refractory bricks, such as silica brick or fire-clay grog.

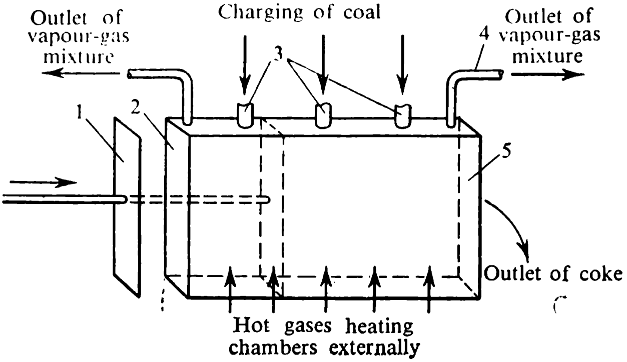

Outlet of vapour-gas mixture
Charging of coal
Outlet of vapour-gas mixture
1
2
3
4
5
Outlet of coke
Hot gases heating chambers externally

Fig. 78. Coking chamber

1—coke pusher; *2*—front wall; *3*—charging holes; *4*—elbow pipe; *5*—rear wall

The coking chamber is a long and narrow rectangular section passage (Fig. 78). Front wall *2* and rear wall *5* of the oven are detachable and are tightly closed during the charging operation. The chamber's roof has charging holes *3* which open when the chamber is charged with coal and closed during the coking period. The gaseous and vaporous products that result from coking are removed from the chamber through walls *4* into gas collectors. Once coking is completed, end walls *2* and *5* are removed by a special mechanism and the coke "cake" of 15 or 16 tons is forced out of the chamber by coke pusher *1*. As the coke is fed, the "cake" disintegrates and lumps of the red-hot coke fall onto the industrial car brought into the chamber, where they are quickly cooled with water to avoid combustion of the coke.

The coke-oven battery generally has more than 60 chambers operating in parallel. Part of the battery is shown in Fig. 79. Passages are formed between chambers *1*. These passages are heating walls *2* along which the hot flue gases are moving (their path is shown by arrows in Fig. 79). These gases give off their heat to the coking coal through the walls.

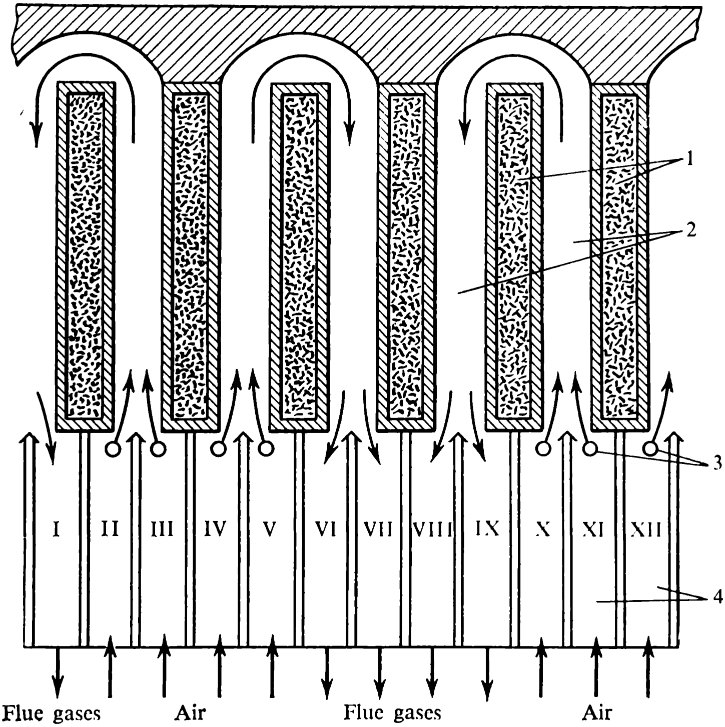


Fig. 79. Coke-oven battery

1—chambers; *2*—heating walls; *3*—holes; *4*—regenerators

Flue gases result from burning gaseous fuels, like blast-furnace, coke-oven or producer gases. A coke-oven battery is fitted with regenerators *4* located under the coking chambers. The heat from gas flowing out of the heating partitions in the regenerators is used to preheat air which is used to burn the gaseous fuel admitted through holes *3*. The air is fed into regenerators *II*, *III*, *IV*, *V*, *X*, *XI*, and *XII* with heated packings. The air is heated in these regenerators and is used for burning gases fed through holes *3*. The flue gases pass along the heating partitions, heat the walls of the coking chambers and the packings of regenerators *I*, *VI*, *VII*, *VIII*, and *IX*, escaping into the stack. Thus, the packings in regenerators *II*, *III*, *IV*, *V*, *X*, *XI*, and *XII* are gradually cooled with air, and the packings of regenerators *I*, *VI*, *VII*, *VIII*, and *IX* are heated with flue gases. This continues for about 15 to 20 minutes, after which the air is fed into regenerators *I*, *VI*, *VII*, *VIII*, and *IX* with heated packings, and the flue gases, into regenerators *II*, *III*, *IV*, *V*, *X*, *XI*, and *XII* with cooled packings.

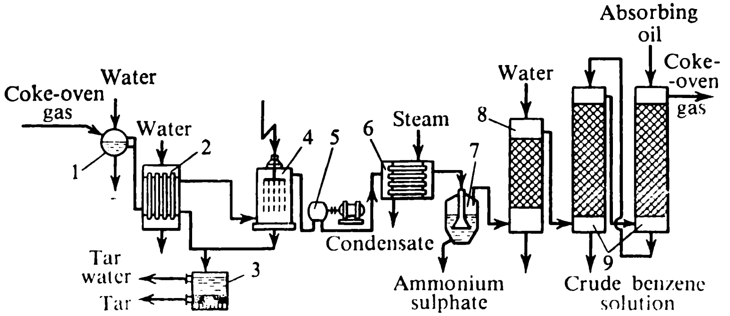
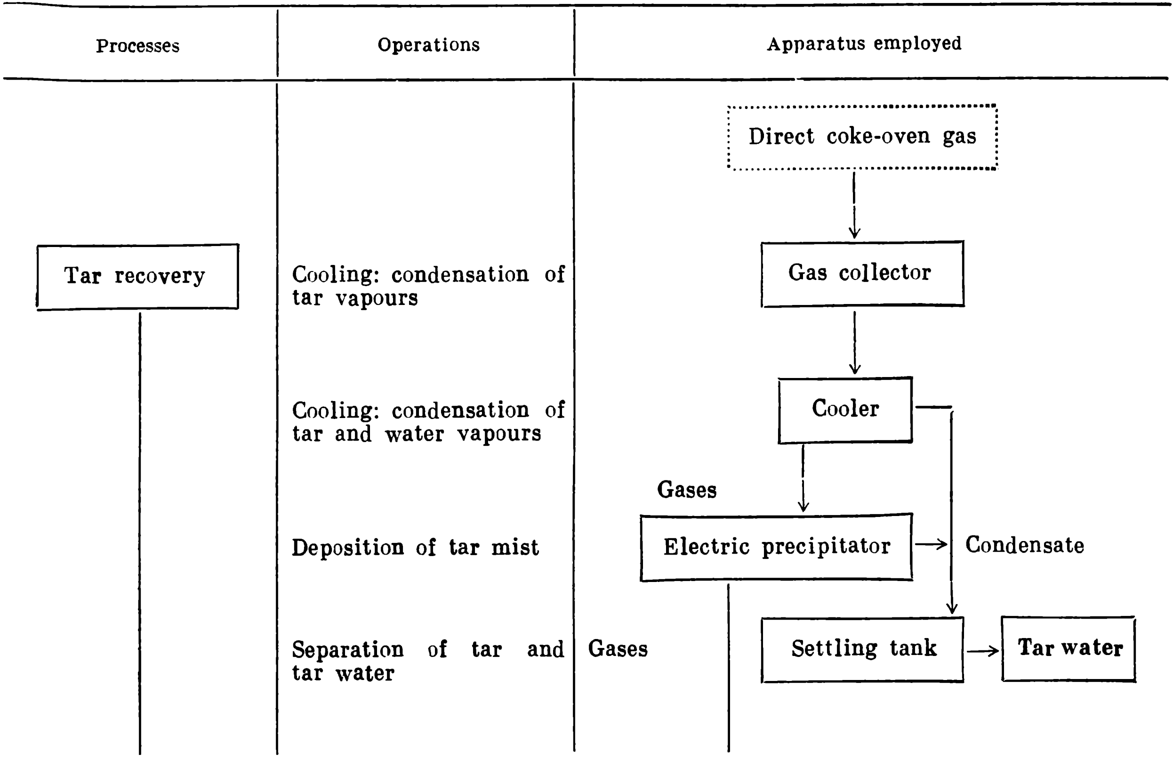


Fig. 80. Processing of direct coke-oven gas

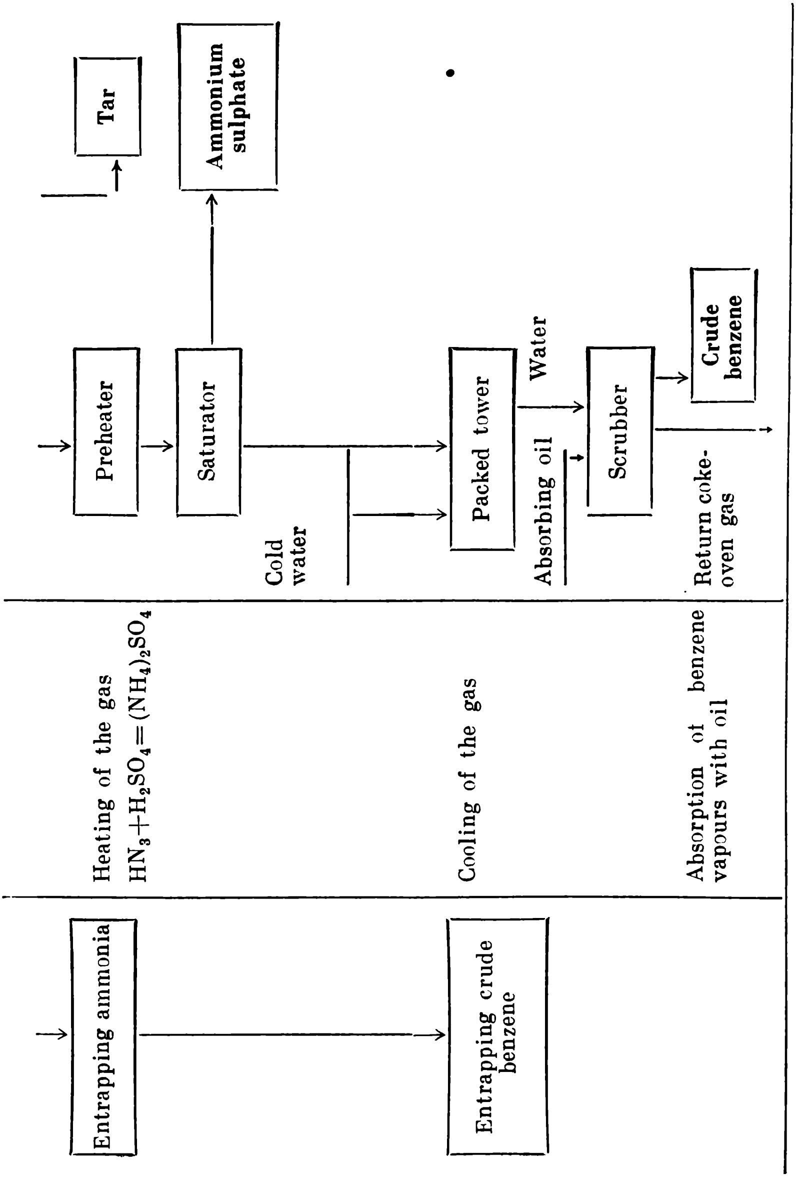
1—gas collector; 2—cooler; *3*—collector; *4*—electric precipitator; *5*—gas exhauster; *6*—preheater; *7*—saturator; *8*—packed tower; *9*—benzene scrubbers

Processing Coke-oven Gases. The coke-oven gas leaving the coking chamber is called a **direct** coke-oven gas. Coal tar, tar water, ammonia, benzene or its homologues, naphthalene, sulphur and cyanogen compounds are recovered directly from coke-oven gas. Freed from these substances, the coke-oven gas, composed basically of hydrogen and methane, is called a **return** coke-oven gas. Coke-oven gas processing is depicted in Fig. 80 and presented in Table 19.

TABLE 19. **Processin of Direct Coke-oven Gases**



Processes	Operations	Apparatus employed
		Direct coke-oven gas
Tar recovery	Cooling: condensation of tar vapours	Gas collector
	Cooling: condensation of tar and water vapours	Cooler
	Deposition of tar mist	Gases Electric precipitator Condensate
	Separation of tar and tar water	Gases Settling tank Tar water


Entrapping ammonia
Entrapping crude benzene
Heating of the gas
$HN_3+H_2SO_4=(NH_4)_2SO_4$
Cooling of the gas
Absorption of benzene vapours with oil
Preheater
Saturator
Tar
Ammonium sulphate
Cold water
Packed tower
Water
Absorbing oil
Scrubber
Crude benzene
Return coke-oven gas

The direct coke-oven gas, after leaving all the chambers, is admitted to gas collector *1* laid along the battery, and water is injected into this gas collector. The gas is then cooled to about 80 °C, coal tar partially condensing on it. Solid coal particles are simultaneously removed in the gas collector. After the gas is cooled to 20-30 °C in cooler *2*, tar and water vapours condensate. The ammonia present in the gas is partially dissolved in the condensed water to form tar water. The tar and the tar water run out from the coolers into collector *3* where they are separated by density. Being heavier, the tar accumulates at the bottom of the collector. The tar present in the gas partially turns into mist which does not settle as the tar condensates in the coolers. The tar mist is removed from the coke-oven gas by settling it in electric precipitator *4* operating at a voltage of 60 000 to 70 000 V. To carry the gas, exhauster (air blower) *5* is installed behind the electric precipitators.

The ammonia contained in the coke-oven gas is dissolved partially in the tar water. The ammonia that remains in the gas after the coolers is entrapped in saturator *7* using tower sulphuric acid which reacts with ammonia to form crystals of ammonium sulphate:

$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4 \qquad (12.1)$$

The process for absorbing ammonia with sulphuric acid is heterogeneous; it involves a gas and a liquid. Therefore, to accelerate the process the surface of contact of the reacting phases should be enlarged. To this end, the saturator is provided with a bubbler which is a jagged pipe immersed in liquid. The gas flows down the pipe, bubbles through the liquid, and is withdrawn at the top of the setup. To increase the rate of reaction (12.1), the gas is heated with steam in tubular preheater *6* before being admitted to the saturator.

The crystals of ammonium sulphate formed in the saturator are withdrawn from the saturator together with the solution. They are separated then by centrifuges, and used as a nitrogen fertilizer.

Freed from ammonia, the coke-oven gas is sent to entrap crude benzene. Entrapping crude benzene by absorbing it with absorbing oils at 20 to 25 °C in scrubbers *9* (packed towers) has the widest applications. Coal-tar oil (a fraction of distilled coal tar that boils at 230 to 300 °C) is used as absorber. The gas admitted to the benzene scrubbers is precooled with water in packed tower *8*. The crude benzene solution in the absorbing oil flows out of scrubbers *9*. Since the crude benzene has a boiling point much lower than that of the absorbing oil, the former is distilled from the absorbing oil which is again fed for spraying the scrubbers.

The *return coke-oven gas* is removed from the scrubbers, and then purified of hydrogen sulphide and other sulphur-containing compounds. The return gas contains 54 to 59% H_2, 23 to 28% NH_4, 5 to 7% CO, 2 to 3% heavy hydrocarbons, 3 to 5% N_2, 1.5 to 2.5% CO_2, and 0.3 to 0.8% O_2. The calorific value of the return gas varies from 16 750 to 17 200 kJ/m^3. Hydrogen that is derived from this gas is used in the synthesis of ammonia.

About 60 products are now recovered from coal tar and crude benzene. This is accomplished either by heating, when some products volatilize and then are entrapped, or by cooling when some compounds crystallize.

During this processing operation, 1 ton of coal yields (kg):

Benzene	3.5	Pyridine	0.02
Toluene	1.5	Naphthalene	2.0
Solvent-naphtha	0.9	Quinoline	0.01
Xylenes	0.7	Anthracene	0.15
Phenol	0.07	Carbazole	0.02
Cresols	0.10		

All these products are used as raw materials for the chemical industry.

At first glance it may appear that the amount of chemical products from coking coal is insignificant. If the scale of coking is taken into account, it turns out that coal processing yields thousands of tons of benzene, toluene, naphthalene, and other compounds. Despite the fact that some of these products are derived from petroleum, coal tar and crude benzene are still the major suppliers of aromatic hydrocarbons for the chemical industry.

After recovering these products from coal tar, there is some amount of *coal-tar pitch*. It is a black and bright mass which is softened by heating, and used in road building, in the manufacture of electrodes, and in other areas.

12.4 Fuel Gasification

Fuel gasification is one of the processes widely employed in fuel processing to produce gases from solid fuel. The gases are an ash-free transportable fuel and the raw material for chemical synthesis.

Gasification is mostly accomplished in gas generators, and the gases they produce are called **producer gases.** To convert the fuel charged into the generator to a gas, air or steam is purged through the gas. Oxygen contained in the air or steam reacts with the carbon of the fuel to form carbon monoxide. As air is purged through the fuel, the following reaction occurs:

$$2C + O_2 \rightleftarrows 2CO + Q \qquad (12.2)$$

The reaction produces a so-called **air producer gas.** According to reaction (12.2), only the oxygen contained in the air reacts with the carbon in the fuel. Atmospheric nitrogen does not react with the carbon in the fuel, remaining unchanged. Therefore, air producer gas theoretically contains only 34.7 per cent by volume CO and 65.3 per cent by volume N_2. This air producer gas is called an **ideal air gas.** Since other reactions occur, except for reaction (12.2), the carbon monoxide content in this gas practically varies from 30 to 32 per cent.

If steam is fed to the generator, **water producer gas** is formed according to the following reaction:

$$C + H_2O \rightleftarrows CO + H_2 - Q \qquad (12.3)$$

It follows from reaction (12.3) that the ideal water gas should theoretically contain equal amounts of CO and H_2, i.e. this gas should contain 50 per cent by volume CO and 50 per cent by volume H_2. In actual fact, the composition differs somewhat from the ideal.

If an air-vapour mixture or an oxygen-vapour mixture is fed to the gas generator, reactions (12.2) and (12.3) occur simultaneously. **Air-vapour** or **semi-water gases** are formed in the first reaction and **oxygen-vapour gases** in the second. Their composition depends on the air-vapour or oxygen-vapour ratio in the blast.

One of the quality indices for producer gases is the amount of heat resulting from the combustion of one cubic metre of the gas and is called the **calorific value**, and expressed in kJ/m^3.

The composition and calorific value of some industrial producer gases are summarized in Table 20.

Table 20 shows that all the producer gases have a relatively high calorific value, and they contain carbon monoxide and hydrogen which act as the initial material for the manufacture of ammonia, alcohols, organic acids, etc. Thus, producer gases are a source of heat energy and raw materials for the chemical industry.

TABLE 20. **The Composition of Producer Gases**

Type of gas	Blast	Gas composition					Calorific power, kJ/m^3
		CO	H_2	CO_2	N_2	Other gases	
Air	Air	32	43	4.2	59	1	4 600
Water	Steam	39	50	5	5	1	10 500
Semi-water	Steam + air	35	36	5	23	1	8 400

To obtain the highest CO and H_2 content in producer gases, the gasification process should be carried out under such conditions so that the equilibria of reactions (12.2) and (12.3) are shifted to the right as much as possible, and so that they occur at the highest rate.

The equilibrium of these reactions depends on temperature and pressure, and their effect is determined by the Le Chatelier principle. For example, low temperatures are required to improve the degree of gasification during the exothermic reaction (12.2), and high temperatures for the endothermic reaction (12.3). According to the Le Chatelier principle, increased pressure shifts the equilibrium of reactions occurring with a decrease in the volume to the right. Since both reactions (12.2) and (12.3) occur with an increase in the volume, it is undesirable to carry them out under increased pressure.

Kinetics, i.e. the gasification rate, determines, to a very large degree, the result of the process. The process of gasification of a solid fuel is said to be heterogeneous, a solid substance reacting with a gas. Therefore, the process rate is affected by the rate of the chemical reactions (12.2) and (12.3), the rate of oxygen or steam diffusion from a gas stream, in which the solid particle flows, to its surface, and the surface contact area of the reacting phases.

To make gasification processes proceed at a high speed, they are generally carried out at the high temperature of about 1000 °C. At this temperature, the reaction rate is very high, leaving the major determinant (limit) in the overall gasification rate to be the diffusion rate of the reactants. This process occurs in the diffusion region and the basic way to intensify the process is to increase the rate of the gas stream. This process is considerably intensified when the fuel is ground, to increase the surface of the reacting phases.

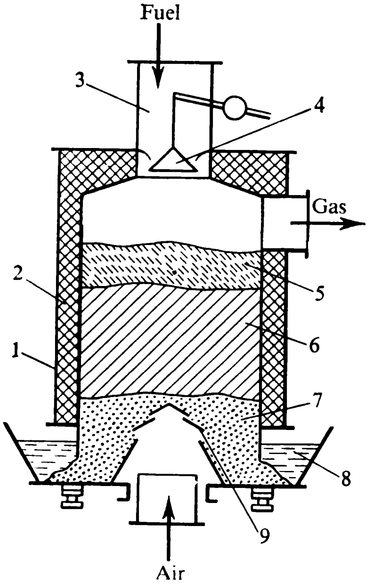


Fig. 81. Gas generator

1—steel shell; 2—lining; 3—charging box; 4—seal cone; 5—predrying zone; 6—gasification zone; 7—ash; 8—ash bowl; 9—fire grate

CO and H_2 resulting from reaction (12.3) may react to form methane. For example:

$$C + 2H_2 \rightleftharpoons CH_4 + Q \tag{12.4}$$

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O + Q \tag{12.5}$$

These reactions occur with a decrease in the volume. Therefore it is advisable to employ increased pressures to shift the equilibrium to methane formation.

At a pressure of about 25 kgf/cm^2, a methane-rich producer gas can be obtained by gasification. Since methane has a high calorific value, a producer gas is formed. A large amount of heat—16 000 kJ/per cubic metre of the gas—is liberated during the combustion of the producer gas. However, generators operating under increased pressures are costly to manufacture and service.

The *gas generator* (Fig. 81) is the basic apparatus for the gasification processes. It is a vertical cylindrical apparatus. The cylinder is steel shell *1* lined with refractory brick *2*, since the gasification process is carried out at high temperatures, of about 1000 to 1100 °C. The gas generator walls are immersed in ash bowl *8* which is filled with water and is slowly revolving. Fire grate *9* is also revolving together with the ash bowl. Blast, such as air, is fed to the bottom of the gas generator through this fire grate. The fuel is periodically admitted through charging box *3* with conical seal *4* lowered, and it is gradually moving downwards, i.e. the phases are moving in counterflow. First, the fuel is predried by the rising gases in predrying zone *5* and then oxidized, as shown in reaction (12.2), in gasification zone *6*. The resulting producer gas is removed from the top. Ash *7*, which remains after gasification, is admitted to ash bowl *8* and withdrawn from the apparatus.

Fluidized-bed fuel gasification is effected in a gas generator. Its construction is similar to that of an oven intended to calcine pyrite in a fluidized bed.

A fine-grained fuel (the developed surface of the phase contact) is placed onto the grid of such a generator, and the blast is fed at a high rate under the grid. The resulting gas is removed from the top. Generators of this type are highly efficient and allow gasifying finely grained fuel which cannot be used in filter-bed generators. Fluidized-bed generators are disadvantageous in that a large amount of coal dust and ash are carried away together with the gas, and special devices are required to entrap them.

12.5 Wood Processing

Wood processing is one of the oldest chemical technological processes. Ancient Egyptians derived charcoal from wood, to recover metals from ores. At the present time, wood processing has become an independent branch—the wood-chemical industry.

The chemical composition of wood is very complex and differs in various wood species. Therefore, processing various softwood and hardwood species produces various products. Cellulose, hemicellulose, and lignin are the basic substances constituting the vegetable tissue. The mineral substances form ash.

Cellulose $(C_6H_{10}O_5)_n$ has a fibrous structure. It is insoluble in water and organic solvents. Cellulose is dissolved using mineral acids. The cellulose content varies from 30 to 50 per cent in dry wood and more than 90 per cent in cotton.

Hemicellulose is composed of pentosans $(C_6H_8O_4)_n$ and hexosans $(C_6H_{10}O_5)_n$, which are less stable than cellulose and are more readily dissolved by acids. Dry wood is 24 to 30% hemicellulose.

Wood contains 25 to 30 per cent of *lignin*. The structure of lignin is yet to be determined.

Resins are extracted from wood. Rosin and turpentine, also tanning and other agents are obtained from resins.

There are two types of processes in wood processing: the pyrogenic process (pyrolysis or dry distillation of wood) and the chemical process (treatment of wood with solutions of weak acids or alkalis at relatively low temperatures).

Dry distillation of wood is similar to coal coking. Wood is heated in the absence of air to 400-470 °C, causing solid, liquid, and gaseous products, as in the case of coking, to form. However, the composition of these products and their amounts are other than those during coal coking.

Dry distillation of wood produces a solid product, such as charcoal; liquid products, such as tar water and resin; and gases.

Charcoal has found important industrial application. Its yield is as low as 32 to 38 per cent by weight of the wood being processed. Charcoal is used instead of coke to smelt high-grade cast iron, because it contains no impurities, such as sulphur and phosphorus, harmful to cast iron. Charcoal is used to manufacture electrodes for electric furnaces and electrolytic cells, activated carbons for gas masks, and to clean gases from harmful impurities.

Tar water contains methanol CH_3OH, acetic acid CH_3COOH, acetone $(CH_3)_2CO$, furfural $(C_5H_4O)_2$, and other compounds which are derived from tar water and used to synthesize chemical products.

It should be noted that the development of the chemical industry has increased the demand for acetic acid and methanol to such an extent that the wood-chemical industry is not in a position to meet it. This has caused synthetic processes for their manufacture to have found wide application.

Wood tar. Flotation agents essential to ore beneficiation, oil for the wood impregnation, and creosote, a product with a strong antimicrobial effect, are all derived from this tar.

Gases from the dry distillation of wood are used as fuel.

In addition to pyrogenic wood processing, purely chemical processes have found wide application. They are carried out at relatively low temperatures. As a result of wood treatment with chemical agents, these methods are employed to manufacture cellulose, ethanol, and other products.

The Manufacture of Cellulose. Cellulose (compressed cellulose resembles untreated board) is essential in the manufacture of artificial fibres, e.g. viscose rayon fibre, paper, celluloid, cellophane, cine film, and gun powder. One cubic metre of wood produces about 170 to 200 kg of cellulose which in turn can produce about 1500 m of silk cloth.

Cellulose is mostly manufactured from wood, since the cost of cotton is higher than that of wood.

The manufacture of cellulose is done by extracting it from wood, in other words, it is separated from hemicelluloses and lignin. To this end, chopped wood—wood chips—is treated with some agents, for example, with solutions that dissolve the hemicelluloses and the lignin, leaving the cellulose untreated. To dissolve the hemicelluloses and the lignin, weak acid or alkali solutions are used. There are two basic methods to manufacture cellulose; (1) sulphite (acid) and (2) sulphate (alkaline) methods.

In the *sulphite method* wood chips are treated in a slightly acidic solution of calcium bisulphite, $Ca(HSO_3)_2$, containing dissolved sulphur dioxide, SO_2 at temperatures no higher than 135-145 °C and pressures 5 to 7 kgf/cm^2 for 10 to 15 h. During the cooking process the cellulose undergoes almost no change, whereas the hemicelluloses and the lignin pass into solution. The cellulose is then separated from the solution, called a *sulphite liquor*, purified from undecomposed wood or other inclusions, washed with water, dried, compressed, and delivered to the users.

When cellulose is manufactured by this method, 1 ton of cellulose produces about 10 to 12 tons of sulphite liquors. Efficient use of these liquors is of tremendous importance to the national economy, for when discharged into rivers or other water reservoirs, they do not only pollute them, but also cause great damage to fishery. Processing these liquors yields ethanol, C_2H_5OH, tanning extracts, binding materials for sand moulds, etc.

The *sulphate method* uses a NaOH-containing solution to decompose wood. The cellulose is cooked in this solution at temperatures of 165 to 175 °C and pressures of 8 to 10 kgf/cm^2 for 3.5 to 8 hours. As with the sulphite method, the lignin and the hemicelluloses pass into solution, the cellulose is separated, purified, dried, and compressed. Unlike the sulphite method, liquors obtained by the alkaline method are recycled into the process (regenerated). Powdery Na_2SO_4 is added to these liquors (hence, the name of the method—sulphate), and the mixture is calcined to accomplish this. Calcination and subsequent treatment of the calcined product with lime milk, $Ca(OH)_2$, yield sodium hydroxide which is then recycled into the process to obtain cellulose.

Wood hydrolysis. Processing wood by treating chopped wood with weak acids is called hydrolysis of wood. This is a very promising method. When sawdust or wood chips are treated with 0.3-0.5% sulphuric acid at temperatures of 170 to 180 °C and pressures of 7 to 10 kgf/cm^2, hemicelluloses and cellulose are hydrolyzed, i.e. they add water and are transformed into sugars (saccharification):

$$(C_6H_{10}H_5)_n \xrightarrow{+H_2O} \underset{\text{glucose}}{nC_6H_{12}O_6} \qquad (12.6)$$

The remaining lignin is separated from the solution of sugars and is used as a filler in the manufacture of polymeric materials, such as plastics and rubber.

The solution of sugars is neutralized with lime milk and is directed to fermentation vats where ethanol is synthesized biochemically:

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2 \qquad (12.7)$$

In addition to the ethanol used to manufacture rubber, wood hydrolysis produces alimentary glucose and furfural which are used to manufacture plastics, and also yeast containing proteins and vitamins. These are a valuable fodder for animals, birds, and fish. One ton of wood can produce 150 to 180 litres of 95% ethanol, 30 to 40 kg of yeast, and 4 to 7 kg of furfural.

REVIEW QUESTIONS

1. How are fuels classified? What are solid fuels composed of?
2. What is the essence of the coking process? What products does it yield?
3. Explain the operation of the coking chamber according to Fig. 78.
4. Draw the coke-oven gas processing diagram.
5. What process is called gasification?
6. Draw a diagram for gas generator.
7. Write the reactions which occur when fuels are gasified with air or steam (at atmospheric pressure and increased pressure).
8. Name the basic components of wood.
9. What is the essence of the dry distillation of wood? What products do we derive in this case?
10. What properties of cellulose are essential for the extraction from wood?

Chapter 13

PROCESSING LIQUID FUELS (PETROLEUM AND PETROLEUM PRODUCTS)

Petroleum has been used since ancient times. Russian 16th century chronicles note that during Boris Godunov's reign "hot thick water" was brought from Ukhta to Moscow. Until the second half of the 19th century, petroleum had been mainly used as a fuel burned in furnaces. From the second half of the 19th century plants were constructed to extract kerosene from petroleum. Kerosene was used for lighting purposes. Petrol, lighter than kerosene, was discharged or burned. As mechanical engineering developed considerable amounts of lubricating oils were needed which, in addition to kerosene, began to be derived from petroleum. Yet, petrol was not still used.

From the beginning of the 20th century, motor vehicles and then airplanes were rapidly developed, and petrol became an essential product for them. Petroleum processing became more "profound", petrol became one of the basic products from petroleum processing. Other products, such as ligroin, kerosene, and lubricating oils were obtained simultaneously with petrol. Kerosene ceased to be used for lighting purposes when electricity began to be used instead. At the present time kerosene is used in jet aviation, and for tractor and diesel engines. The emergence of new technology called for using various lubricating oils and other petroleum products.

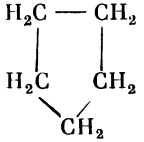
Since the 1930s, in addition to various types of fuel and lubricating oils, products, such as ethylene, propylene, butanes, butylenes, phenol, and benzene began to be derived from petroleum. These products are essential for the chemical industry. Petroleum processing has turned out to be the most complicated industrial branch—*the industry of petrochemical synthesis.* Petrochemical plants are highly automated enterprises fitted with modern equipment. Various types of fuels and raw materials for the manufacture of plastics, synthetic rubbers, chemical fibres, and detergents are derived from petroleum at these enterprises.

13.1 The Composition and Properties of Petroleum

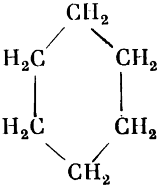
Petroleum is an oily liquid. It is lighter than water and has a hue anywhere from light yellow to dark brown or almost black. Petroleum predominantly consists of 85-86 per cent of carbon or 12-14 per cent of hydrogen that are interbonded to form various chemical compounds—hydrocarbons. In addition to hydrocarbons, substances containing oxygen, nitrogen, sulphur, and mechanical impurities are found in small amounts in petroleum.

The *hydrocarbon part* of petroleum consists of C_nH_{2n+2} paraffinic (saturated), naphthenic (cyclic hydrocarbons having the general formula C_nH_{2n}), and aromatic hydrocarbons. Unsaturated C_nH_{2n} hydrocarbons are generally not present in petroleum, but are contained in the products of petroleum refining.

CH_4 to C_4H_{10} paraffinic hydrocarbons are gaseous products. They are present in petroleum in dissolved state. During petroleum production, when the petroleum pressure decreases, these hydrocarbons are evolved as casing-head gases from the petroleum. Liquid paraffinic hydrocarbons, C_5H_{12} to $C_{16}H_{34}$, constitute the basic mass of the liquid portion of petroleum and liquid fractions that result from petroleum processing. Solid $C_{16}H_{34}$ or higher paraffinic hydrocarbons are found in the dissolved state in petroleum, and can be derived from them. Naphthenic hydrocarbons in petroleum are mainly the derivatives of cyclopentane



and cyclohexane:



Aromatic hydrocarbons are present in petroleum in relatively small amounts as benzene or its homologues, such as toluene and xylenes.

Petroleum is subdivided into **paraffinic** (Baku and Embin), **naphthenic-paraffinic** (Grozny and Surohan), **naphthenic-aromatic** (Maikop), some **paraffinic-naphthenic-aromatic** (Maikop) depending on the predominant type of hydrocarbons present.

The *non-hydrocarbon part* of petroleum consists of sulphur, oxygen, and nitrogen compounds.

Petroleum is subdivided by the sulphur content into **low-sulphur** (the Caucasus) with as much as 0.5 per cent of sulphur and **multisulphur** with more than 0.5 per cent of sulphur.

Naphthenic acids, phenols, and resinous substances are oxygen compounds. They impart a dark tint to petroleum, are decomposed, and cokable by heating.

Mechanical admixtures, water, mineral salts, and ash are mineral impurities.

Mechanical admixtures are solid particles of sand and clay that are carried out of the Earth with a stream of petroleum. Water is present in petroleum in two forms. One that is separated from petroleum by settling, and stable emulsions which can be destroyed only by special methods. Mineral salts, for example, calcium or magnesium chloride are dissolved in the water contained in petroleum. The ash content in petroleum is in the hundredth or even thousandth fractions of a per cent.

Petroleum composition determines its physical properties: colour, density, and temperature under which petroleum inflames and solidifies.

The colour of petroleum changes from bright yellow to dark brown. The density of most petroleum varies from 0.83 to 0.97 g/cm^3 at 20 °C. The viscosity of petroleum is not similar and sharply decreases as the temperature rises. The solidification temperature varies within wide ranges between 10 °C and —20 °C. It determines the conditions under which petroleum loses its fluidity. The heat of combustion of petroleum varies from 39 800 to 44 000 kJ/kg.

13.2 Products from Petroleum Processing

Petroleum processing yields the following products: liquid and gaseous fuels, solvents, lubricating oils, greases, solid and semisolid mixtures of hydrocarbons (paraffins, ceresine, petrolatum, etc.), petroleum asphalts and pitches, petroleum acids and their derivatives (naphthanate soaps, sulphonic acids, fatty acids, etc.), and individual hydrocarbons (gaseous and liquid hydrocarbons, such as ethylene, propylene, methane, benzene, toluene, xylene) which are the raw materials for the chemical industry.

Liquid petroleum fuels are subdivided into motor petrols, tractor fuels, diesel fuels, boiler fuels, fuels for jet and turbojet engines.

Liquid fuels are consumed in huge amounts especially as motor petrols used in internal combustion engines. They should contain no sulphur compounds, organic acids or other substances that will corrode metals used to manufacture engines and containers. They should be stable during storage.

Petrols have a fractional composition which determines the beginning and end of the boiling of fractions obtained during petrol distillation within temperature ranges between 25 and 200 °C. The pressure of saturated petrol vapours, i.e. the vapour pressure which exists above liquid petrol, should not exceed the specified limit under specified conditions.

Antiknock properties or detonation stability are the major characteristic of petrols.

Petrol is now used for automobile engines and propeller-driven aeroplane engines (carburettor engines). During operation of such an engine, a combustible mixture of petrol vapours and air is admitted to the engine cylinder, compressed there by the piston and ignited by a spark plug. The products resulting from the combustion of petrol vapours in the interior of the cylinder expand and move the piston. The piston movement is transmitted to the running gear of the machine. The more the mixture is compressed in the engine cylinder or, as they say, the higher its compression ratio, the more economical the engine is. What restricts an increase in the compression ratio? As the compression is increased there comes a point when a further increase in compression causes a sharp increase in the propagation rate of the flame in the engine cylinder, like an explosion, instead of the desired gradual combustion. This process is called **detonation**. It is accompanied by a sharp knock in the cylinder and appearance of black smoke in the exhaust. Detonation increases fuel consumption, reduces engine power, and increases wear.

The tendency of petrol to detonate is characterized by the **octane number**. The higher the octane number of petrol, the lower its tendency to detonation and the better the quality. The octane number is a conventional value. Isooctane (2,2,4-trimethylpentane) has a low tendency to detonate and therefore its octane number is assigned to be 100. The octane number of *n*-heptane, which is highly detonable, is generally assigned to be 0. The octane number of a mixture of isooctane and *n*-heptane varies from 0 to 100, depending on the isooctane content (in per cent) in the mixture. The octane number of a mixture is taken as equal to the isooctane content in this mixture. For example, if a mixture contains 70 per cent of isooctane and 30 per cent of *n*-heptane, the octane number of the mixture is 70. To determine the octane number of petrol, its detonation properties are compared under certain conditions with various mixtures of isooctane and *n*-heptane. Petrol has an octane number corresponding to the isooctane content in the mixture whose detonation properties are similar to those of isooctane. For example, the octane number (76) of automobile petrol indicates that it possesses the same detonation properties as a mixture composed of 76 per cent of isooctane and 24 per cent of *n*-heptane.

Aviation petrol is manufactured to have an octane number of 100 or higher. The higher the octane number of aviation petrol, the smaller amount is required during flight, enabling the airplane payload to be increased. The octane number of a motor fuel increases, as the content of isoparaffins and aromatic compounds increases.

To increase the octane number of a motor fuel, a mixture of petrol and high-octane components, such as isooctane, isopentane, and ethyl benzene, is used, or antiknock agents are added to petrol. Tetraethyl lead $Pb(C_2H_5)_4$ mixed with ethyl bromide and monochloronaphthalene (an ethyl liquid) is an antiknock agent.

Tractor fuel is generally kerosene; its quality is defined by the same properties as that of petrol.

Diesel fuel includes kerosene, gas oil, and solar distillate; it is usable in internal combustion engines.

Boiler fuel includes fuel oil and other petroleum residues.

Jet fuel is a kerosene fraction used in air-jet engines.

Gaseous petroleum fuels include casing-head gases and gases resulting from the processing of petroleum and petroleum products.

Lubricating oils are subdivided into the following groups depending on their application: industrial oils, such as spindle and machine oils; motor oils and aviation oils; for internal combustion engines; transmission oils; turbine oils; compressor oils; cylinder oils for steam machines; and special-purpose oils. The quality of oils is characterized by lubricating power, viscosity, solidification temperature and flash point, density, water content, acidity, cokability, ash content, and stability.

13.3 Petroleum Processing

Petroleum processing is a very complicated process that is preceded by a special treatment.

Petroleum Preparation. The necessity for the preparation of petroleum for processing purposes can be explained by the following reasons.

Sand, clay, water, and other substances in their way are carried away by petroleum fountains flowing out of boreholes. Petroleum contains dissolved gases, water, and salts All these must be removed from petroleum, since their presence disturbs the process of petroleum refining.

Petroleum preparation begins at the oil fields. From the boreholes the petroleum flows along pipes into traps where the dissolved (casing-head) gases are separated, then the petroleum enters settling tanks. Sand and other solid impurities settle to the bottom of the settling tanks, where water is also accumulated, being heavier than petroleum. From the settling tanks, the petroleum is sent to reservoirs from which it is carried out along pipelines or in tank wagons to refineries.

At the refineries, the petroleum is completely dehydrated, the dissolved salts and mechanical impurities are removed from it, and only after this, the petroleum is processed.

Petroleum Processing Methods and the Principal Apparatus. Petroleum-processing methods may be divided into two groups: physical (primary) and chemical (secondary).

Physical petroleum processing *methods* are based on the use of differences in the physical properties of substances incorporated in the petroleum, For example, some of these substances solidify or crystallize at higher temperatures, while other substances, at lower temperatures; some are soluble in some solvents more readily than in other solvents. Should petroleum be heated, various products evaporate from it as the temperature rises. First, the products that boil and evaporate at temperatures lower than those at higher temperatures will volatile from the petroleum. This process is called **petroleum distillation** and it has found the widest application of the different physical methods. No chemical reactions are used in physical refining methods.

Chemical petroleum processing *methods* are based on the fact that hydrocarbons contained in the petroleum and petroleum products undergo the most profound chemical transformations under the effect of temperature, pressure, and catalysts. Numerous chemical reactions occur in these processes to form new compounds and new products.

Although the nature of physical and chemical processes is essentially different, there are some similarities in their practical implementation. Both have two basic operations, **heating** the processible raw material to high temperatures and **separating** the resulting products.

In addition to heating the raw materials, the chemical processes can use catalysts. Petroleum and petroleum products are heated in tubular furnaces.

Tubular flameless combustion furnaces (Fig. 82) are manufactured from prefabricated ribbed panels. Heat-insulating brickwork is laid between the panel ribs. This brickwork maintains the temperature of the external surface of the walls at about 45 °C. Raw materials move along the tubes connected in series. First, it passes along tubes *6*, then is admitted into tubes *2*, *1*, and *5* and, heated to high temperature, is removed from the furnace. The furnace uses a gaseous fuel which is fed into burners mounted in the furnace walls. During the flameless combustion of gaseous fuel in the burners, the burner plates become heated and radiate heat intensively onto the surface of tubes *1*, *2*, and *5*. Flue gases resulting from the combustion give off heat to the raw material that is fed into tube *6* for processing, and escape into the stack. Modern tube furnaces are characterized by their high degree of utilization of the heat from the flue gases and the heated raw material for steam production.

The total length of the tubes is about 1 km and as the petroleum moves along them, during the distillation period, it becomes heated, to about 320 to 350 °C, and when chemical processing methods are employed, the petroleum is heated to still higher temperatures. At high temperatures, the greater part of the petroleum turns into vapours. The vapours and the unevaporated part of the petroleum are admitted to distillation columns to extract some products from them.

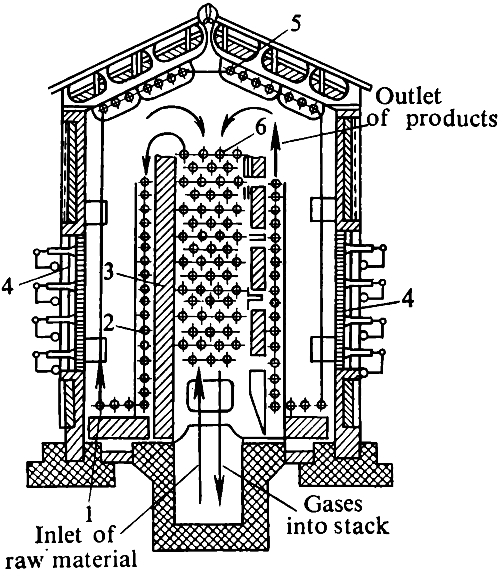


Fig. 82. Tubular furnace for flameless combustion

1, *2*, *5*, and *6*—tubes; *3*—wall; *4*—burners

The distillation column used to separate petroleum products is a steel cylinder not more than 40 m high and with a diameter of 3.5 or 4 m. The interior of the column accommodates several scores of horizontal shelves or trays. One of the tray constructions in the distillation column is shown in Fig. 83. In the centre of the column the tray mounts the vertically directed tube (branch pipe) *1* closed on top with jagged cap *3*. Rising upwards in the column, petroleum vapour passes through the branch pipes and caps. The top of the column is sprayed with a cold liquid, such as petrol, and the liquid flows from tray to tray through overflow pipes *2* (overflow sleeves). Because the overflow sleeves rise over the tray surface, a layer of liquid is always on the tray where the rising vapours bubble through. Although there are other types of distillation columns, their basic operating principle does not differ from that in Fig. 83.

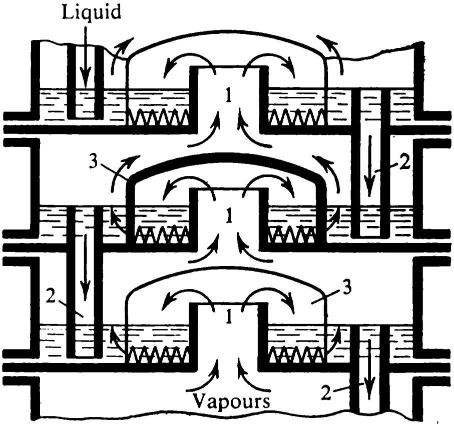


Fig. 83. Distillation column trays
1—branch pipes; *2*—overflow pipes; *3*—bubble caps

A mixture of vapours and liquid flowing out of the tubular furnace are admitted to the bottom of the column. The vapours rise upwards. The temperature decreases the higher up they go in the column, as they move from tray to tray, gradually condensing and giving off their heat to the run-off liquid. This heat causes the easiest boiling products to evaporate from the liquid. Thus, the liquid flowing from tray to tray becomes rich in more high-boiling products, and the vapours, vice versa, in low-boiling products,

Physical processes. As has been noted, distillation is one of the widely used petroleum processing methods. The petroleum distillation process is•depicted schematically in Fig. 84. The petroleum fed to tubular furnace *1* first passes through heat exchangers *4* in which it is heated to 180 °C with the products flowing out of distillation column *2*. The petroleum is further heated to 320 to 350 °C in the tubular furnace to form a vapour-liquid mixture which is fed into distillation column *2*. Steam is fed to the bottom of the column in which the petroleum is separated into fractions or distillates which are removed consecutively along the height of the column.

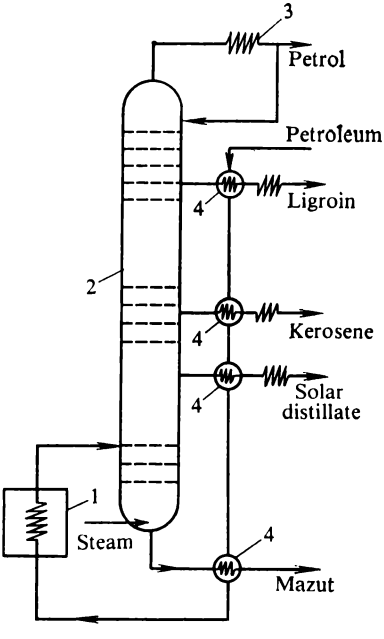


Fig. 84. Diagram of petroleum distillation

1—tubular furnace; *2*—distillation column; *3*—cooler; *4*—heat exchangers

Petrol vapours are removed from the top of the column. They are cooled in cooler *3*. During cooling, the petrol vapours condensate and are transformed into liquid petrol which is then partially stored and partially fed for spraying the column. During petroleum distillation, the petrol yield varies between 3 to 15 per cent by weight of the petroleum being processed. The other distillation products, such as ligroin, kerosene, solar distillate and mazut, are removed from the column, cooled in heat exchangers and pumped into storage sites. The heaviest product—mazut—is removed from the bottom of the column. Its heat is used in heat exchanger *3* for heating the petroleum.

Mazut is not the final petroleum distillation product, A plant almost identical to that in Fig. 84, but operating under rarefaction, may be used to distillate the mazut into fractions to obtain the lubricating oils required to lubricate the moving parts of machines and mechanisms. The residue resulting from the mazut distillation process is called asphalt and is used in road building.

Mazut is frequently called a boiler fuel because it is burned in boiler furnaces and in other furnaces. However, this is not its sole application. Besides lubricating oils, chemical processing of mazut yields petrol and gaseous hydrocarbons which are raw materials for chemical synthesis.

During petroleum distillation, the chemical yield depends on the natural properties of the petroleum; it can be as little as 3 to 15 per cent. It is very important to note the fact that there are no products that can be raw materials for the chemical industry. Chemical processes are free from these disadvantages.

Chemical processes have a number of advantages as compared with physical processes. For example, the petrol yield is 40-50, or higher than 70 per cent. In addition to petrol, gaseous hydrocarbons are obtained that are raw materials for the chemical industry. Some chemical processes allow producing not only gaseous raw materials, but also liquid aromatic hydrocarbons, such as benzene and xylene. Their "flexibility", i.e. the possibility of producing large amounts of petrol and other chemical products, has made chemical processes one of the basic methods for processing petroleum and petroleum products.

Not only petroleum, but also fractions resulting from the petroleum distillation—from ligroin to mazut—are used as raw materials in chemical processes.

Chemical processes are subdivided into three groups: thermal processes where raw material is transformed at high temperatures, thermal catalytic processes carried out at high temperatures and in the presence of catalysts, and low-temperature catalytic processes carried out only in the presence of catalysts.

Thermal processes include thermal cracking, coking, and pyrolysis.

During thermal processes, petrol and other products are produced by transforming the hydrocarbons in the starting material. These transformations are done by high-temperature splitting (cracking) of hydrocarbons with a large molecular mass to form hydrocarbons•with a smaller molecular mass which are contained in the resulting petrol and gases. Although cracking is a rather complex process, it is still possible to establish some regularities in the behaviour of some hydrocarbon groups at high temperatures.

Paraffinic (saturated) hydrocarbons are hydrocarbons that act as raw materials for chemical synthesis.

Unsaturated C_nH_{2n} hydrocarbons resulting from cracking react with each other and with the starting products to form aromatic and other complex hydrocarbons.

Reactions (12.1), (12.2), (12.3), and (12.4) are reversible endothermic reactions. Therefore, according to the Le Chatelier principle, high temperatures are required to shift the equilibrium to form products lighter than the starting products. Hence, higher temperatures reduce the strength of hydrocarbons. On heating, hydrocarbons having long chains are primarily split. Higher temperatures cause the shift of the rupture point of the chain from the middle to the edge, i.e. the yield of gaseous products increases.

The transformation rate of some hydrocarbon groups is different: paraffinic hydrocarbons are decomposed at the highest rate, followed by naphthenic hydrocarbons, and aromatic hydrocarbons being split at the lowest rate. Therefore, when heated, paraffinic hydrocarbons are primarily cracked, followed by naphthenic hydrocarbons and finally by aromatic hydrocarbons; this causes their accumulation in the cracking products.

Reactions (12.1), (12.2), (12.3), and (12.4) occur with larger volume. Hence, higher pressures shift the equilibrium of these reactions from the right to the left to form heavy hydrocarbons.

Thermal cracking is carried out at plants more complicated than tubular plants for petroleum distillation. Yet they are identical in that raw materials are heated in tubular furnaces, and the products are separated in distillation columns. However, cracking conditions differ from those in petroleum distillation. Thermal cracking is mostly carried out at temperatures from 470 to 540 °C and at pressures from 40 to 60 kgf/cm^2. Under these conditions, the splitting reactions occur in liquid and vapour phases. This cracking process is called **liquid-phase cracking**. If the cracking process is carried out at 550 °C and at pressures 2 to 5 kgf/cm^2, the reactions occur in the vapour phase. This process is called a **vapour-phase one**.

The petrol yield is 30 to 35 per cent, that of gases, 10 to 15 per cent, the cracking residue usable as a boiler fuel, 50 to 55 per cent by weight of the raw material. Thermal cracking petrols have octane numbers higher than some petroleum distillation petrols, i.e. 60 to 70 units, but they are less stable than petroleum distillation petrols.

Coking of heavy petroleum raw materials (petroleum residues) is carried out at temperatures between 510 and 530 °C. High processing temperatures promote a more profound cracking of the hydrocarbons to obtain a high yield of coke and gases. For example, coking one of petroleums at 533 °C yielded 10.1 per cent of gas, 63 per cent of gas oil (liquid product), 14 per cent of coke, and 0.9 per cent of waste products.

Coking is generally used to obtain high-quality coke required to manufacture electrodes, carbides, and carbon sulphide. The other coking products are also used.

Pyrolysis is the most rigid form of thermal processes. The raw materials usable in pyrolysis may include low-octane petrols, kerosene fractions, and petroleum residues. Pyrolysis is effected at temperatures between 700 and 900 °C and at a pressure close to atmospheric. Ethylene and propylene, unsaturated gaseous hydrocarbons, are produced under these conditions. Resins are also formed which contain considerable amounts of aromatic compounds, such as benzene, toluene, and xylene. Thus, pyrolysis yields the raw material required to manufacture a number of chemical products, such as synthetic resins, synthetic fibres, and rubbers. Therefore, the development of pyrolysis is inseparably linked with the development of the petrochemical industry, for which pyrolysis has been one of the basic sources of raw materials in the recent years.

Thermal catalytic processes include high-temperature processes that occur in the presence of catalysts, namely: catalytic cracking and catalytic reforming.

Catalytic cracking has found wide application. Petroleum processing products, such as gas oil, are used as the raw material.

Catalytic cracking is generally carried out at temperatures between 450 and 500 °C and at atmospheric pressure in the presence of catalysts. Alumosilicate catalysts, such as solid and porous bodies composed predominantly of alumina Al_2O_3, proved to be most effective. The petrol yield in the presence of these catalysts is as high as 70 per cent of the weight of the raw material being cracked. Catalytic cracking petrols have high octane numbers of 90 to 92 units and do not change their properties during storage. In addition to petrols, catalytic cracking produces hydrocarbon-containing gases; their yield amounts to 12 to 15 per cent of the weight of the raw material.

Thus, catalytic cracking makes it possible to obtain large amounts of high-quality petrols and also considerable amounts of gases.

However, catalytic cracking has a substantial disadvantage since the catalysts very quickly become unserviceable or, as they say, they lose their activity. Catalytic activity is lost by coke depositing on the catalyst surface during cracking. To regain catalytic activity, the coke should be removed from the catalyst surface. This process, called **catalyst regeneration,** is accomplished by burning the coke out when air at temperatures between 550 and 600 °C is passed over the catalyst. Hence, the catalytic cracking process comprises alternating the working process when the raw material to be cracked passes over the catalyst, and the catalyst regeneration process by blowing air.

Catalytic cracking is generally done in continuous-action catalytic reactors which have two parts, a reactor and a regenerator. Hydrocarbon splitting occurs in the presence of a catalyst in the reactor. This reduces the catalyst activity. During the air blowing operation, catalyst activity is regained in the regenerator. The catalyst circulates continuously between the reactor and the regenerator.

Fluidized-bed cracking, which has found the widest application, uses a reactor and a regenerator which are combined in a single apparatus and is presented in the diagram in Fig. 85. The upper portion accommodates reactor *6* and the lower portion, regenerator *9* which are interconnected with catalyst conduits *3* and *4*. The raw material leaving the tubular furnace entrains the regenerated catalyst from cylindrical well *2* and is carried along the pipe to reactor grid *7*. The cracking products are freed of catalyst particles in cyclone *5* and then separated. The used catalyst moves down along pipe *4* into the regenerator in which air is blown under grid *1* where the coke is burned out. After purification in cyclone *8*, the flue gases resulting from the combustion process are withdrawn from the apparatus into the boiler, and the regenerated catalyst is recycled to the reactor.

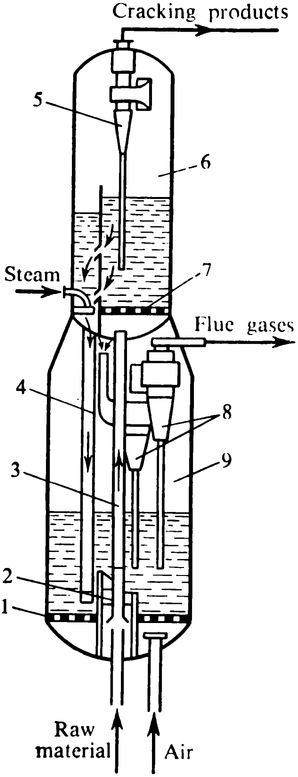


Fig. 85. Fluidized-bed catalytic reactor

1, *7*—grids; *2*—cylindrical well; *3*, *4*—catalyst conduits; *5*, *8*—cyclones; *6*—reactor; *9*—regenerator

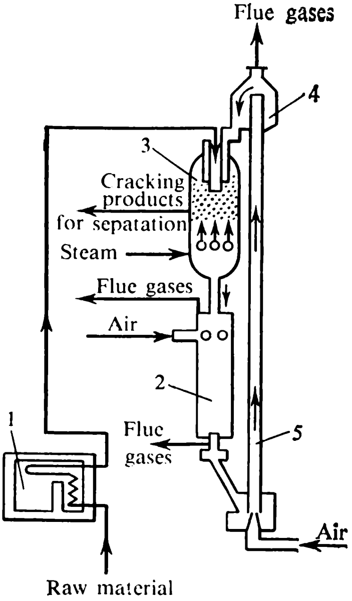


Fig. 86. Moving-bed catalytic reactor

1—tubular furnace; *2*—regenerator; *3*—reactor; *4*—bin; *5*—air hoist

Moving-bed cracking also circulates the catalyst between the reactor and the regenerator. The raw material heated in tubular furnace *1* (Fig. 86) is fed to the top of reactor *3* into which the regenerated catalyst is admitted from bin *4*. The products from the cracking process are withdrawn from the top of the reactor and are then separated. The used catalyst is taken from the catalytic reactor at the bottom and is admitted to regenerator *2* where the coke is burned off the catalyst surface. The combustion products then leave the regenerator. The regenerated catalyst is fed from the bottom of the regenerator through air-lift *5* by compressed air forced with an air blower into bin *4*.

Reforming. Reforming is a type of cracking that differs from conventional cracking by the raw material used. When reforming is carried out, the raw material includes low-octane petrols or ligroins from which either high-octane petrols or the raw materials for the chemical industry are derived. This process makes it possible to increase the octane number of petrols from petroleum distillation and thermal and catalytic cracking. In addition, the raw materials for the chemical industry can be obtained.

Catalytic reforming processes, like **platforming**, have found the widest application. The catalyst of this process is platinum applied to the surface of alumina. If platforming is carried out at temperatures between 480 and 510 °C and at pressures between 15 and 30 kgf/cm^2, the raw materials such as benzene, toluene, and xylene are obtained. If this process is carried out at a pressure of about 50 kgf/cm^2, high-octane petrols are produced that have an octane number of about 98 without the addition of an ethyl liquid, or higher than 100 with the addition of an ethyl liquid.

In addition to the liquid products, catalytic reforming yields gases usable in the synthesis of ammonia, methanol, and other compounds. During catalytic reforming, the yield of gases is 15 per cent of the weight of the raw material.

13.4 The Purification of Petroleum Products

Purification is the final stage in the manufacture of motor fuels and lubricating oils. This stage is essential, since the products resulting from the distillation and cracking processes contain reactive unsaturated hydrocarbons, sulphur and nitrogen compounds. They render petroleum products unstable, promote the appearance of a dark colour and unpleasant odour, and they deposit in engine cylinders. There are chemical and physicochemical methods for the purification of petroleum products.

Chemical methods include purification with sulphuric acid and treatment with hydrogen, hydrocleaning, and **physicochemical** methods include adsorption and absorption purification methods.

Purification with sulphuric acid comprises mixing the product with a small amount of 90-93% sulphuric acid at room temperature. Chemical reactions produce the purified product and so-called acid petroleum asphalt into which undesirable impurities penetrate. Acid petroleum asphalt, industrial waste, may be used to manufacture sulphuric acid. Sulphuric acid purification is a cumbersome process involving the formation of waste and the use of large amount of reactants.

At the present time, a *hydrogenation method* or *hydrofining* has been widely used. Hydrogen reacts with sulphur, nitrogen- and oxygen-containing compounds in the presence of an alumo-cobalt-molybdenum catalyst at temperatures from 380 to 420 °C and at pressures from 35 to 40 kgf/cm^2 to form readily-removable hydrogen sulphide, ammonia, and water. Unsaturated compounds are simultaneously hydrogenated to make the product more stable. Hydrofining makes it possible to use high-sulphur petroleums to obtain petroleum products.

Adsorption purification methods are based on adsorption (with a solid substance) of harmful impurities contained in petroleum products. The adsorbent (solid adsorbent) is mostly natural clays. Clays are added to the petroleum product, stirred up, and then separated from the petroleum product or the petroleum products are filtered through the clays.

Absorption purification methods utilize the selective ability of some liquids to dissolve harmful substances contained in the petroleum products. Nitrobenzene, furfural, liquid sulphur dioxide, and dichloroethyl ether are used for this purpose. A high-quality purified product is obtained.

13.5 The Processing of Gases

The Soviet Union has huge reserves of combustible natural gases. In some cases, these are *natural gases* which are to be found in the thickness of sedimentary rock, and in other cases, *casing-head gases* that are dissolved in petroleum and rise to the surface together with it.

In addition to natural and casing-head gases, large amounts of gases are manufactured at refineries, petrochemical plants, and gas generator stations. Gases are not only the cheapest and convenient fuel, but also a valuable raw material for the chemical industry. Natural and casing-head gases contain hydrocarbons, such as methane CH_4, ethane C_2H_6, propane C_3H_8, butane C_4H_{10}. Refinery and coke-oven gases additionally contain ethylene C_2H_4, propylene C_3H_6, and butylenes C_4H_8. Producer gases contain carbon monoxide and hydrogen. These substances are the raw material for the manufacture of fertilizers, plastics, chemical fibres, synthetic rubbers, solvents, and detergents. To manufacture these products, gases should be processed. The gas processing methods may be subdivided into three groups:

(1) the direct use of substances incorporated into the gases by adding oxygen (oxidation), chlorine (chlorination), water (hydration), hydrogen (hydrogenation); removing hydrogen (dehydrogenation), adding CH_3, C_2H_5 groups to the molecules (alkylation), changing the structure of the molecules (isomerization), combining many simple molecules into complex molecules (polymerization), etc.;

(2) cracking of the hydrocarbons incorporated into the gases to produce unsaturated hydrocarbons (olefins);

(3) conversion by reacting with steam to produce carbon monoxide and hydrogen.

When these processes occur, a great variety of products can be derived from gases. The great economic effect of the utilization of gases should be noted. For example, 200 man-h are required to manufacture 1 ton of ethanol from 9.6 tons of potatoes, and only 10 man-h, from 0.8 ton of ethylene.

Gaseous raw materials are important for the chemical industry. Their use has caused new technological processes, equipment and flow diagrams to be created, and made it possible to make cheaper the cost of some chemical products.

REVIEW QUESTIONS

1. Name the basic types and composition of petroleum.
2. How are tubular furnaces constructed?
3. What is the purpose of distillation columns and how are they constructed?
4. What products are obtained from petroleum processing?
5. What is the octane number of petrol?
6. What process is called petroleum distillation? Draw up its diagram.
7. What are the advantages of chemical methods of processing of petroleum and petroleum products as compared with petroleum distillation?
8. Write the basic cracking reactions.
9. By referring to Figs. 85 and 86, explain the operation of catalytic reactors.
10. What is the purpose, and how are petroleum products purified?

Chapter 14

TECHNOLOGY OF BASIC ORGANIC SYNTHESIS

14.1 Products and Raw Materials for Basic Organic Synthesis

The industry for basic (heavy) organic synthesis produces the major organic substances that act as starting materials (intermediate products) for obtaining more complex organic compounds, or they are used independently in the national economy.

The products of basic organic synthesis are organic substances that are relatively simple structurally: hydrocarbons, alcohols (methanol and ethanol), aldehydes and ketones (formaldehyde, acetic aldehyde, acetone), chloroderivatives (dichloroethane and vinyl chloride), carboxylic acids (formic and acetic) and their derivatives (esters and acetic anhydride), and diene hydrocarbons and their derivatives (butadiene and chloroprene).

Products of basic organic synthesis are used to manufacture plastics and resins, synthetic rubbers and chemical fibres, organic dyes and paintwork materials, pharmaceuticals and photomaterials. They are used in the manufacture of plant control agents, solvents and detergents, lubricants and flotation agents, various auxiliary materials for some industries in the national economy.

During the developmental years of the organic synthesis industry, vegetable and animal raw materials (such as wood in the manufacture of acetic acid and methanol; sugary substances in the manufacture of ethanol, etc.) and also processed coal-tar products (such as benzene, toluene, etc.) were used to obtain organic compounds. Later on, calcium carbide CaC_2 (in the manufacture of acetylene, C_2H_2) and producer gases containing carbon monoxide, which is one of the major starting compounds of organic synthesis, began to be used as the raw materials.

At the present time, numerous products of basic organic synthesis are derived from hydrocarbon gases. Paraffinic hydrocarbons (methane and its homologues), olefins (ethylene, propylene, *n*-butylene, *iso*-butylene), diolefins (divinyl and isoprene), acetylenic hydrocarbons (acetylene), aromatic compounds (benzene, toluene, naphthalene) are the major raw materials for the modern industry of basic organic synthesis. Petroleum, natural gases and their processed products are the inexhaustible source of hydrocarbons.

In many cases, chemical transformations occur in a single stage when manufacturing products of basic organic synthesis.

Numerous reactions occurring during syntheses may be reduced to some types of reactions that are most frequently used. These include oxidation and reduction, dehydrogenation (detachment of hydrogen) and hydrogenation (addition of hydrogen), hydration (addition of water), sulphonation (addition of a sulphonic group, SO_3H), nitration (addition of a nitric group, NO_2), polymerization (the combination of similar molecules into a single molecule), isomerization (the change in the structure of molecules without any change in their composition). Examples given below illustrate the production processes based on a certain typical reaction.

14.2 Dehydrogenation of Hydrocarbons

During **dehydrogenation** there occurs a rupture of the bond between the carbon and hydrogen atoms in the hydrocarbon molecule and hydrogen detaches from the molecule of the organic compound. This process is generally carried out at high temperatures. But such temperatures make it possible to break the bond between the two carbon atoms, i.e. splitting of hydrocarbons (cracking) occurs. In order to carry out the preferred dehydrogenation of hydrocarbons, rather than their cracking, some special techniques are employed. They include raising the temperature, reducing the pressure, selecting a certain residence time of reactants in the reactor, and adding selective catalysts. The catalysts cannot completely suppress the reactions of hydrocarbon splitting, but they do increase the dehydrogenation reaction rate by many times. This makes it possible to carry out the dehydrogenation process for a shorter period of time than it takes for the splitting reaction to occur.

The Manufacture of Acetylene by Methane Cracking. Acetylene, C_2H_2, is a colourless gas having a slight peculiar odour. It is an unsaturated compound with a triple bond, $HC{\equiv}CH$. It readily enters into a great variety of chemical reactions to form numerous derivatives which are starting compounds for the manufacture of major chemical products, such as synthetic rubbers, resins, and plastics. For example, acetaldehyde which is processed into acetic acid, ethanol, butadiene, ethyl acetate, vinyl chloride, vinyl acetate, and chloroprene is derived from acetylene. Acetylene is used to achieve high temperatures which are required for cutting and welding metals (autogenous welding). When acetylene burns in oxygen, a flame of about 3200 °C can be obtained.

Acetylene is produced by high-temperature treatment (up to 1500 °C) of methane hydrocarbons (methane, ethane, and also a mixture of hydrocarbons contained in natural gas). In this case, dehydrogenation of saturated hydrocarbons occurs and they are converted to acetylene:

$$2CH_4 \rightarrow HC{\equiv}CH + 3H_2 - Q \tag{14.1}$$

$$C_2H_6 \rightarrow HC{\equiv}CH + 2H_2 - Q \tag{14.2}$$

An increase in the temperature and a decrease in the pressure enhance the yield of acetylene. To create high temperatures, part of methane is burned up in a furnace (oxidized with oxygen):

$$CH_4 + 0.5O_2 \rightleftarrows CO + 2H_2 + Q \qquad (14.3)$$

High temperatures (1400 to 1500 °C) are maintained in the furnace as heat evolves. The unburned methane is decomposed at these temperatures to form acetylene. This process is called the **thermooxidative pyrolysis of methane.**

Figure 87 shows a simplified diagram for the furnace in which thermooxidative pyrolysis of methane occurs. The preheated methane and oxygen are admitted to the top of furnace *1*, where they are mixed. Plate *2* from a refractory material having a great number of holes is mounted at the lower edge of the lined portion of the furnace. The methane-oxygen mixture passes through the holes, and methane conversion occurs under the plate. To obtain a high yield of acetylene and to avoid complete decomposition of methane accompanied by carbon evolution, gases should be present in the high-temperature zone for a very short period of time. Water is therefore injected under plate *2*. When contacted with the reaction products, the water sharply reduces the temperature of the gases.

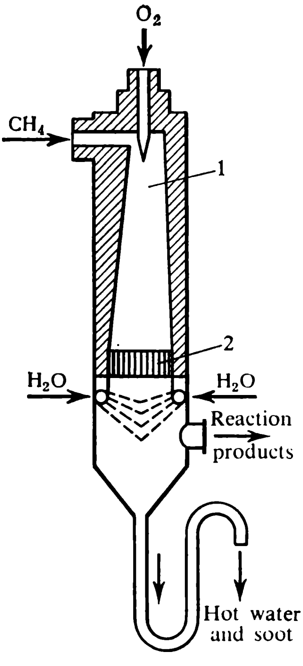


Fig. 87. Furnace for the thermooxidation pyrolysis of methane

1—furnace; *2*—plate

Due to incomplete conversion of methane and the occurrence of side reactions, a complex gas mixture is formed at the furnace outlet. The mixture comprises C_2H_2, H_2, CO, CO_2, H_2O, the C_2H_2 content being about 8-10 per cent.

To derive acetylene from the thermooxidative pyrolysis gases, selective solvents, e.g. dimethylformamide and *n*-methylpyrrolidon-2-one (those dissolving only acetylene) are used.

The Manufacture of Butadiene (Divinyl). Butadiene is a hydrocarbon with two double bonds $CH_2{=}CH{-}CH{=}CH_2$. It is one of the basic substances in rubber manufacture. It can be obtained by dehydrogenation of butane, C_4H_{10}, according to the following reaction:

$$CH_3-CH_2-CH_2-CH_3 \rightleftharpoons CH_2=CH-CH=CH_2+2H_2-Q \qquad (14.4)$$

According to the Le Chatelier principle, the equilibrium degree of conversion is increased by lowering the pressure and raising the temperature. In industry, the process is carried out at atmospheric pressure and at temperatures between 550 and 575 °C, using alumochromium catalysts (in fluidized-bed reactors).

Butadiene (divinyl) may also be manufactured by simultaneously dehydrogenating and dehydrating ethanol, C_2H_5OH (according to the Lebedev method) in the presence of catalysts such as zinc oxide and alumina:

$$2CH_3-CH_2-OH \xrightarrow{400-450\ ^\circ C} CH_2=CH-CH=CH_2+H_2+2H_2O \qquad (14.5)$$

The flow diagram for the manufacture of divinyl from ethanol is presented in Fig. 88 and Table 21. Ethanol is evaporated in alcohol evaporator *1* and fed into a catalytic reactor, such as retort furnace *4*. The alcohol vapours are preheated in coiled pipe *2* and admitted to retort *3*, steel pipes 4 or 5 m high filled with a catalyst. The retorts are located at the hot-red walls of furnace *4* being heated during the combustion of a fuel. The divinyl obtained in the furnace is separated from the gas mixture by cooling and absorption. The gas mixture leaving the furnace *4* is cooled in condensator cooler *5*, and after the unreacted alcohol is separated in separator *6*, the mixture is directed to absorption column *7* filled with a ceramic packing (in the form of rings). To absorb the divinyl, the column is sprayed with cooled ethanol.

After heating in heat exchanger *8*, the resulting ethanolic butadiene solution is sent for fractionation to tray-type column *9* where the solution is separated into butadiene (the top of the column) and alcohol (the bottom of the column). The alcohol flowing out of the bottom of column *9* is cooled in heat exchanger *8* giving off its heat to the solution fed for fractionation and is again sent to spray absorption column *7* for entrapping the divinyl.

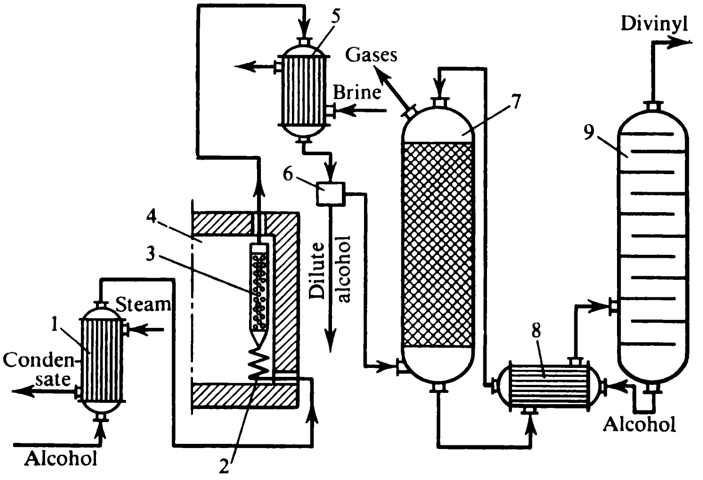
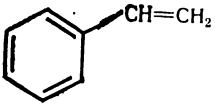


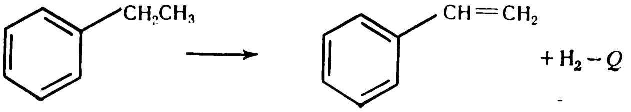
Fig. 88. Diagram for manufacturing divinyl

1—alcohol evaporator; *2*—coiled pipe; *3*—tubes; *4*—retort furnace; *5*—cooler-condenser; *6*—separator; *7*—absorption column; *8*—heat exchanger; *9*—distillation column

The Manufacture of Styrene (Vinyl Benzene or Phenyl Ethylene). Styrene



is the major starting product for the manufacture of rubbers and plastics. Styrene is obtained by dehydrogenation of ethyl benzene:



(14.6)

TABLE 21. **Manufacture of Divinyl**

Process	Operation	Apparatus used
		Ethanol
Preparation of alcohol-air mixture	Heating and evaporation of alcohol	Alcohol-evaporator
Preparation of divinyl	$2CH_3-CH_2-OH \rightarrow$ $\rightarrow CH_2=CH-CH=CH_2+H_2+$ $+2H_2O$	Retort furnace (catalytic reactor)
Recovery of divinyl	Cooling	Condense-cooler

Absorption of divinyl with alcohol

Heating of divinyl solution with alcohol

Separation of divinyl and alcohol

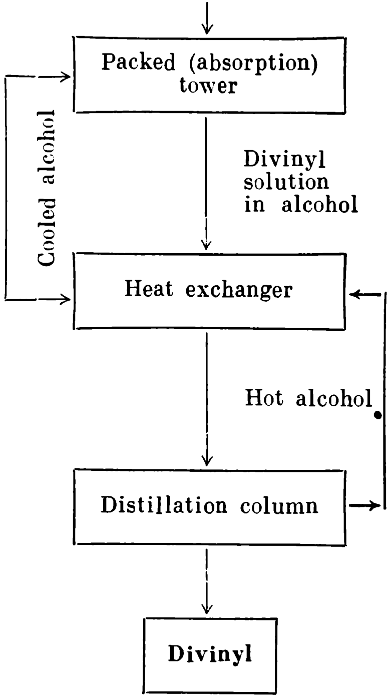
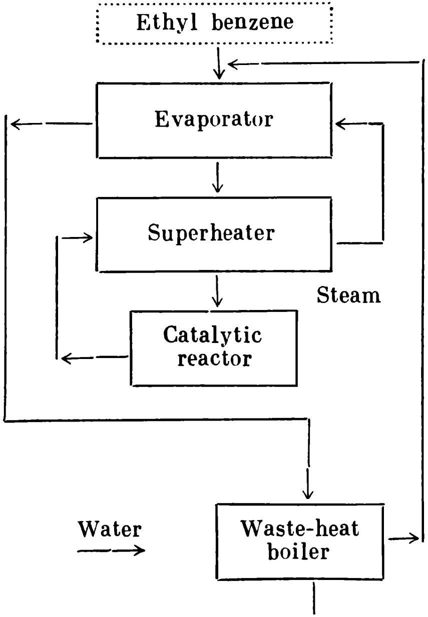
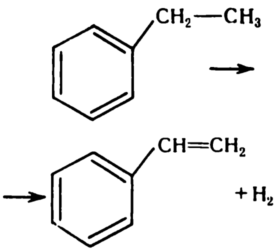
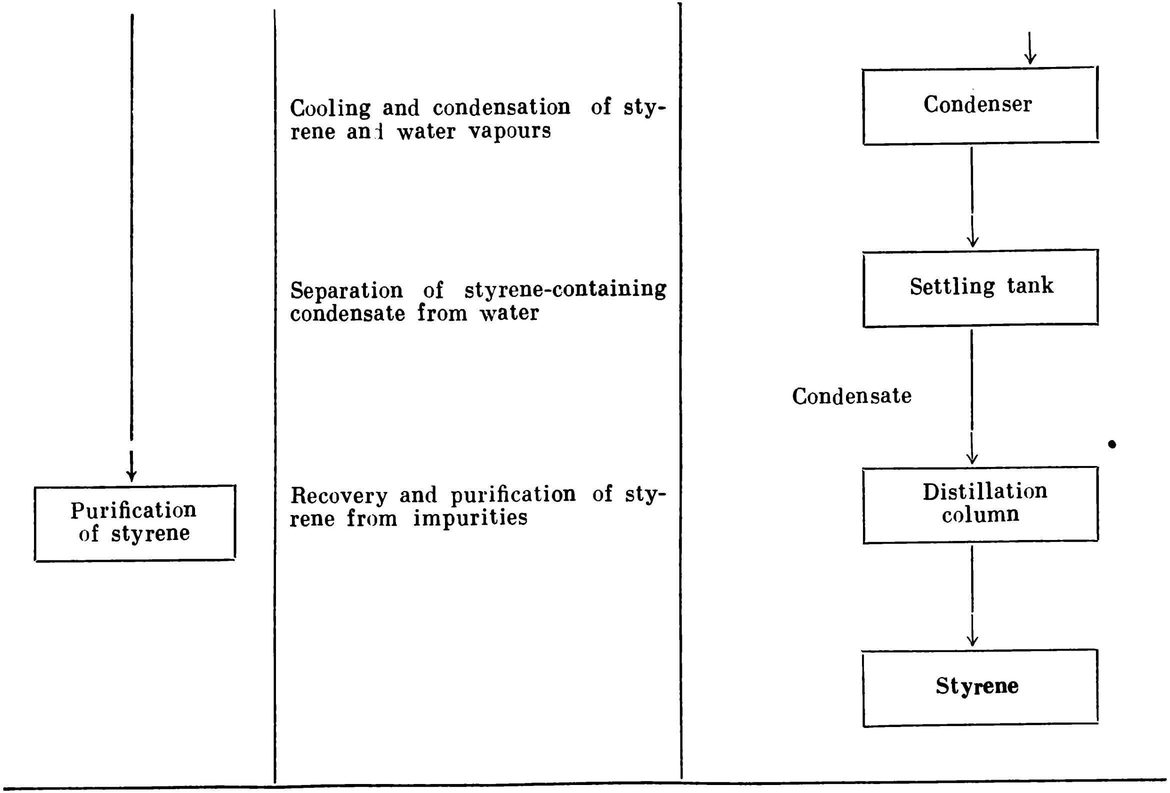


TABLE 22. **Manufacture of Styrene**

Process	Operation	Apparatus employed
Preparation of ethyl benzene	Evaporation of ethyl benzene	 Ethyl benzene Evaporator Superheater Steam Catalytic reactor Water Waste-heat boiler
Preparation of styrene	Heating of ethyl benzene vapours Dehydrogenation of ethyl benzene 	
Recovery of styrene	Cooling of gases to form steam from water	



Cooling and condensation of styrene and water vapours

Separation of styrene-containing condensate from water

Recovery and purification of styrene from impurities

Industrially, dehydrogenation of ethyl benzene is effected at temperatures from 560 to 600 °C in the presence of a catalyst (iron, zinc or magnesium oxides) in tubular and shaft reactors. The flow diagram for the manufacture of styrene is shown in Fig. 89 and Table 22. Water vapour derived from water in waste-heat boiler *4* is mixed with ethyl benzene and passed through evaporator *3* and superheater *2*. There it is heated to 530 °C and admitted to catalytic reactor *1*. The heat which is essential for carrying out endothermic dehydrogenation reactions is supplied by superheated steam. The hot gases leaving catalytic reactor *1* pass successively through superheater *2*, evaporator *3*, and waste-heat boiler *4* where they give off their heat to the reactants admitted to reactor *1*. From waste-heat boiler *4* the cooled gases are admitted to condenser *5* in which water and styrene-containing hydrocarbons condense. The styrene-containing condensate is separated from water in settling tank *6*. The uncondensed gases are used as a fuel. The catalyst is regenerated when the latter is blown with air.

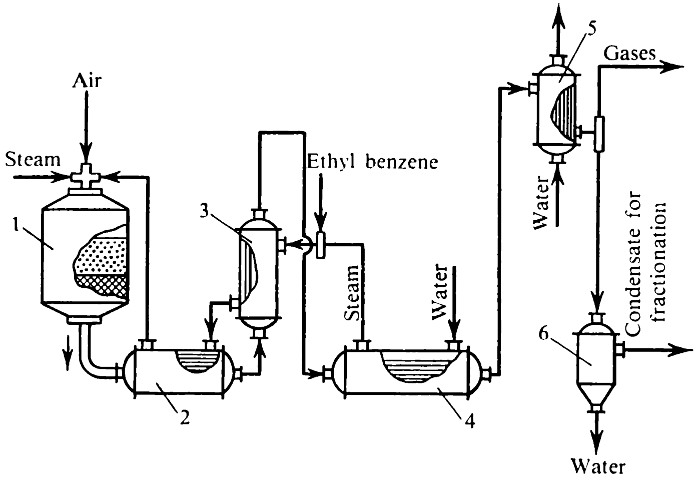


Fig. 89. Diagram for manufacturing styrene

1—catalytic reactor; *2*—superheater; *3*—evaporator; *4*—waste-heat boiler; *5*—condenser; *6*—settling tank

14.3 Hydrogenation Processes

Many industries for basic organic synthesis are based on hydrogenation processes. **Hydrogenation** occurs when hydrogen is added to carbon-containing compounds with or without recovery of water. Hydrogenation reactions are exothermic and occur only in the presence of catalysts, frequently at considerable hydrogen pressure.

Among hydrogenation processes, the interaction of carbon monoxide with hydrogen is of special importance. Carbon monoxide and hydrogen may give various compounds, such as methanol, formic aldehyde, hydrocarbons, and other compounds depending on the conditions. During hydrogenation of carbon monoxide, catalysts are widely used that have selective properties; they accelerate one of the probable reactions of carbon monoxide with hydrogen. These catalysts include metals, such as iron, nickel, cobalt, copper, and oxides of magnesium, aluminium, and thorium. The reaction can be directed as desired to obtain some product by selecting certain catalysts, temperatures, pressures, and carbon monoxide and hydrogen volume ratio.

Methanol Synthesis. Methanol CH_3OH is a colourless, transparent, poisonous liquid having a weak odour and miscible with water in any ratios. The boiling point of methanol is 64.7 °C and melting point is 95 °C. Its density is 0.796 g/cm^3. Methanol was formerly obtained only by dry distillation of wood (wood alcohol). As the chemical industry (mostly organic synthesis) made progress, the consumption of methanol has grown considerably. It is employed as a solvent, an additive to a motor fuel, and as the raw material for the manufacture of chemical products, such as formaldehyde and methyl ether, and acrylic acid. These in turn are essential to the manufacture of plastics, antiknock mixtures, varnishes, and dyes.

At present, methanol is mainly manufactured by synthesis from carbon monoxide and hydrogen. The manufacture of synthetic methanol relates to large-ton (producing large amounts of the product) industries of basic organic synthesis. The basic reaction in the synthesis of methanol is as follows:

$$CO + 2H_2 \rightleftarrows CH_3OH + Q \qquad (14.7)$$

In addition to this main reaction, some side reactions may occur.

To increase the yield of the desired product (methanol), a selective-action zinc-chromium catalyst is used. Such a catalyst considerably increases the main reaction rate (14.7) and does not accelerate or accelerates only slightly side reactions. The side reactions are therefore suppressed.

The reaction that produces methanol is reversible and exothermic, forming methanol with a large reduction of volume. Hence, the reaction equilibrium shifts to form methanol at elevated pressures and lower temperatures. At the same time, the synthesis of methanol is exceedingly slow at ordinary temperatures. Therefore, to accelerate it, the process is carried out at a high temperature of about 400 °C.

To shift the equilibrium towards formation of methanol, the process is carried out with excess hydrogen against the stoichiometric value (1 : 4 CO to H_2 ratio) and at a pressure of about 250 kgf/cm^2.

Methanol is synthesized at high space velocities of the gas, 10 000 to 35 000 $m^3/m^3 \cdot h$. This improves catalyst intensity.

The use of the rather high temperature of 400 °C to ensure a high process rate has an unfavourable effect on the position of the reaction equilibrium. Therefore, the methanol concentration in the gases at the catalytic reactor outlet is as low as 5 to 20 per cent per passage of the gas mixture through the catalyst bed. After methanol separation the unreacted gases are returned to the process, i.e. a cyclic flow diagram is used for the synthesis of methanol.

It is apparent from these physicochemical conditions that the manufacture of this product is identical with the synthesis of ammonia. This similarity can also be seen by comparing the flow diagrams for their manufacture.

The flow diagram of the methanol synthesis from carbon monoxide and hydrogen is shown in Fig. 90 and Table 23. The synthesis gas purified from impurities is compressed to 250 kgf/cm^2 in compressor *1* and admitted to mixer *2* where it is mixed with a circulating gas supplied by compressor *9*. From the mixer the gas enters filter *3* to be cleaned from oil which gets into the gas mixture during lubrication of the compressor. Then, the gas passes through heat exchanger *4* to be heated to about 220 °C, and then enters synthesis column *5*.

Methanol synthesis is an exothermic process. Heated by the reaction heat, the gas passes from synthesis column *5* through the intertube space of heat exchanger *4* in which the gas is cooled, giving its heat to the gas fed for synthesis. Thus, the process is made autothermic, i.e. the temperature needed to carry out the process is made using the reaction heat itself. From heat exchanger *4* the gas is sent to water condenser cooler *6* and then admitted to separator *7* to separate the condensed methanol. The gas mixture that did not enter into reaction is recycled by circulating compressor *9* for repeated transformation. From separator *7* the methanol is admitted into crude alcohol collector *8*, where it is fed for fractionation to manufacture pure methanol.

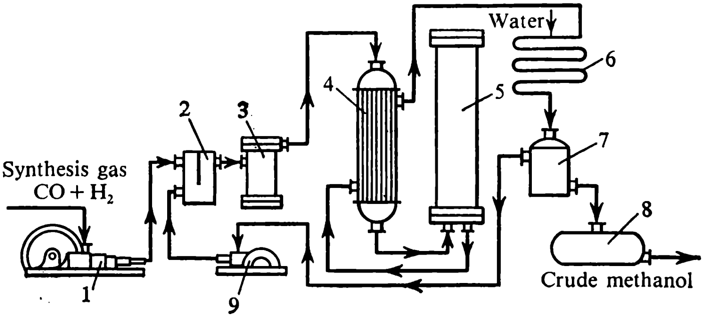


Fig. 90. Diagram of synthesizing methanol

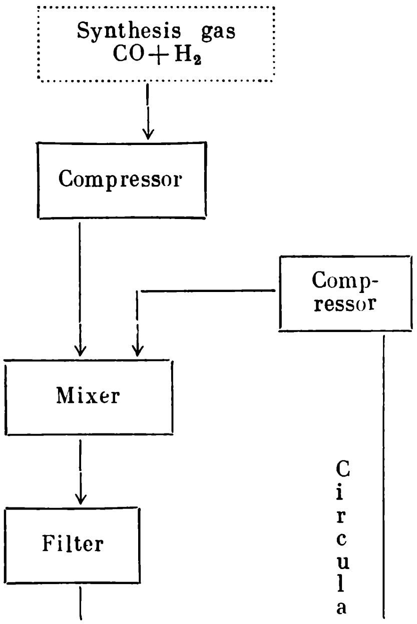
1, *9*—compressors; *2*—mixer; *3*—filter; *4*—heat exchanger; *5*—synthesis column; *6*—cooler-condenser; *7*—separator; *8*—collector

14.4 Hydration of Hydrocarbons

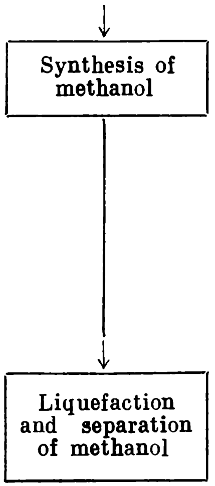
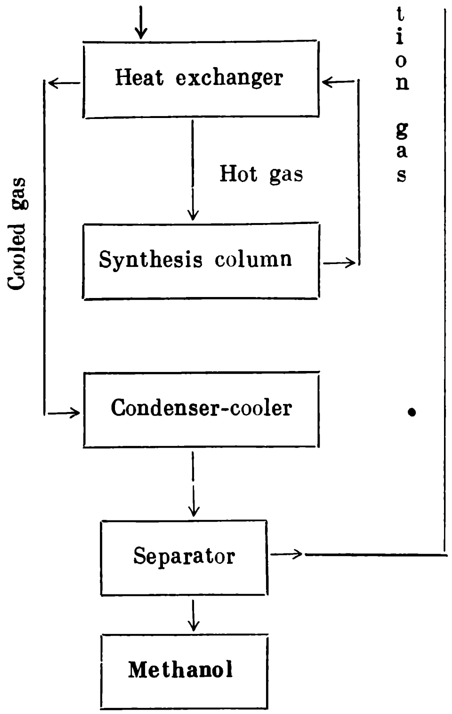
Hydration of unsaturated hydrocarbons (water reacts with olefins in the presence of catalysts) produces monohydric alcohols.

The Manufacture of Ethanol. The boiling point of ethanol, C_2H_5OH, is 78.3 °C and its density is 0.789 g/cm^3 (at 20 °C). Ethanol is a major organic product and manufactured in

TABLE 23. **Manufacture of Methanol**



Process	Operation	Apparatus employed
		Synthesis gas $CO+H_2$
Preparation of gas	Compression of gas	Compressor
	Compression of circulating gas	Compressor
	Mixing with circulating gas	Mixer
	Cleaning from lubricating oil	Filter Circula

 Synthesis of methanol Liquefaction and separation of methanol	Heating $CO + 2H_2 \rightleftharpoons CH_3OH$ Condensation of methanol Separation of methanol and circulating gas	 Heat exchanger Hot gas Synthesis column Cooled gas Condenser-cooler Separator Methanol tion gas

large amounts. It is used to manufacture butadiene which in turn is used to manufacture synthetic rubbers. It is also used as solvent and the raw material in many industries in the national economy, namely: pharmaceutical, perfumery, paint-and-varnish, and food industries, in the manufacture of chloroform, diethyl ether, ethyl acetate, explosives, synthetic fibres, and other organic synthesis products.

Ethanol was formerly manufactured by a biochemical process, i.e. by fermentation using microorganisms of various sucrates contained in edible raw material, such as potato and grain. Great amounts of valuable foodstuffs had to be consumed. Processes for manufacturing ethanol from inedible raw material, and especially the manufacture of synthetic ethanol by hydration of ethylene have acquired a great importance for the national economy.

Water is added to ethylene by direct and indirect methods.

Indirect hydration is carried out in two stages using sulphuric acid to form intermediate products.

Direct hydration of ethylene is a more perfect process in which water is directly added to ethylene in the presence of a catalyst. The hydration process is carried out in vapour and liquid phases according to the following reaction:

$$CH_2{=}CH_2+H_2O \rightleftarrows CH_3{-}CH_2{-}OH+Q \qquad (14.8)$$

In accordance with the Le Chatelier principle, the yield of alcohol increases as the temperature decreases and the pressure rises. However, to increase the reaction rate, the reaction is carried out at temperatures between 280 and 300 °C and at a pressure of 70 kgf/cm^2 in the presence of a catalyst. The catalyst of the vapour-phase process includes phosphoric acid applied onto silica gel, or synthetic alumosilicate.

The schematic flow diagram for the manufacture of ethanol by catalytic hydration of ethylene in a vapour phase is shown in Fig. 91 and Table 24. Ethylene compressed to 70 to 80 kgf/cm^2 by a compressor is fed together with water or superheated high-pressure steam (70 kgf/cm^2), to tubular heat exchanger *1* in which this mixture is preheated with the hot gases leaving catalytic reactor *3*. The preheated mixture passes through tubular furnace *2* at an outlet temperature of 280 °C; the mixture heated to this temperature is admitted into catalyst filled catalytic reactor *3*. There the ethylene hydration reaction occurs. From catalytic reactor *3* the hot ethanol-containing vapour-gas mixture enters heat exchanger *1*. The condensed vapours of water and ethanol are separated in collector *4*. The resulting aqueous solution of crude ethanol containing 15 or 16 per cent of C_2H_5OH is directed from collector *4* for fractionation.

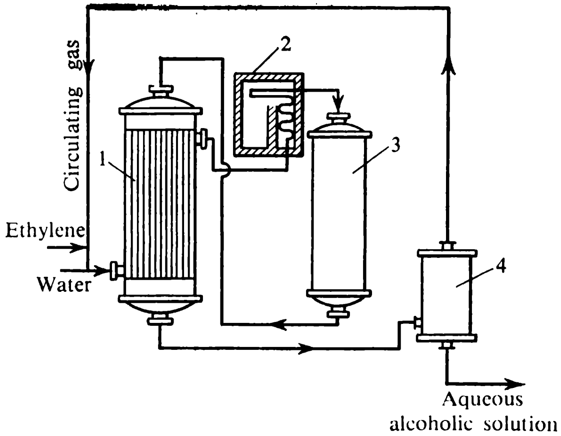
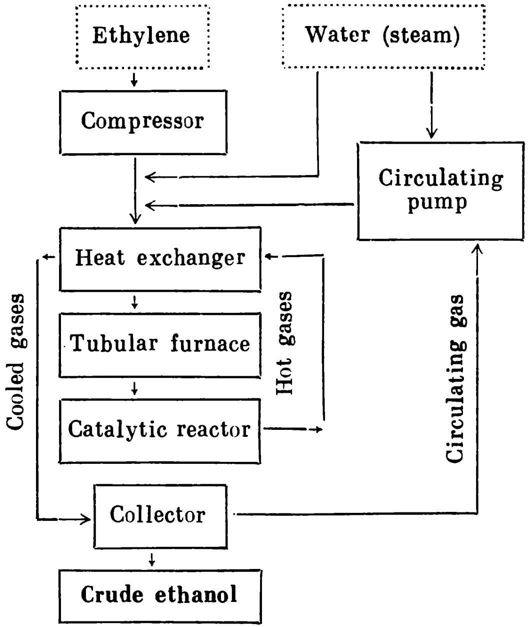


Fig. 91. Schematic diagram for manufacturing ethanol
1—heat exchanger; *2*—tubular furnace; *3*—catalytic reactor; *4*—collector

The gases that remain after separating the crude alcohol in collector *4* contain a large amount of ethylene, since the hydration process does not allow obtaining the degree of conversion higher than 4 or 5 per cent per one pass of the vapour-gas mixture through the catalytic reactor. Therefore, direct hydration of ethylene is effected using a cyclic (circulating) flow diagram. The unreacted gases such as ethylene and impurities (circulating gas) are returned to the process by a circulating pump, adding them to the fresh starting mixture fed to the reaction. The use of a circulating flow diagram increases the degree of conversion of ethylene to ethanol to 95 per cent.

TABLE 24. **Manufacture of Ethanol**

Process	Operation	Apparatus employed
Preparation of raw material	Compression of ethylene	
Hydration of ethylene	Heating of vapour-gas mixture $CH_2{=}CH_2 + H_2O \rightleftarrows$ $\rightleftarrows CH_3{-}CH_2{-}OH$	
Separation of ethanol	Separation of alcohol and circulating gas	

14.5 Oxidation Processes

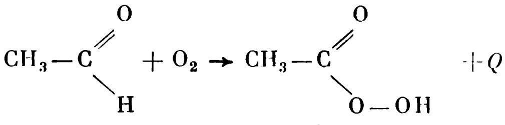
The method for oxidizing hydrocarbons and other organic compounds has been widely employed in modern industrial organic synthesis. This method is used to manufacture alcohols, phenols, aldehydes, ketones, organic acids, and other compounds. Oxidation is effected mostly by air, and in some cases, by oxygen, ozone, and steam, in the presence of catalysts—metals, their oxides, and salts.

The Manufacture of Acetic Acid. Acetic acid, CH_3COOH, is one of the most important organic acids. It plays a tremendous role in the development of many industries. It is used for dyeing fabrics in the textile industry, for manufacturing dyes, in the preparation of esters, preservation and preparation of essences in the food and confectionary industries, in the manufacture of acetyl cellulose, acetate rayon, solvents, plastics, varnishes, acetic anhydride, acetone, and rubber. Anhydrous acetic acid solidifies as colourless crystals at 16.6 °C. Its boiling point is 118.1 °C and density 1.049 g/cm^3 at 20 °C. It is miscible with water and other organic liquids.

From ancient times acetic acid had been manufactured in small amounts as dilute aqueous solution (vinegar) by fermenting ethanol-containing liquids (wine, beer, etc.) in the presence of special so-called acetic bacteria. Dry distillation of wood yields considerable amounts of acetic acid.

However, the greater need for acetic acid caused by the development in the manufacture of acetate rayon and varnishes, in many industries of fine organic synthesis necessitated the manufacture of synthetic acetic acid.

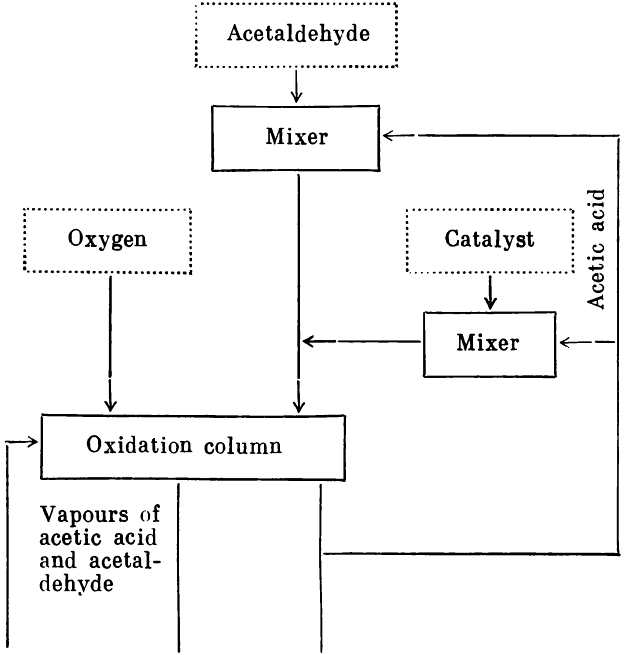
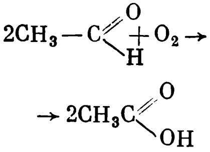
At the present time, oxidation of acetic aldehyde (acetaldehyde) is the major process for producing acetic acid. The oxidation process occurs in the presence of oxygen in two stages: the acetaldehyde is first oxidized to form an unstable intermediate product, peracetic acid:

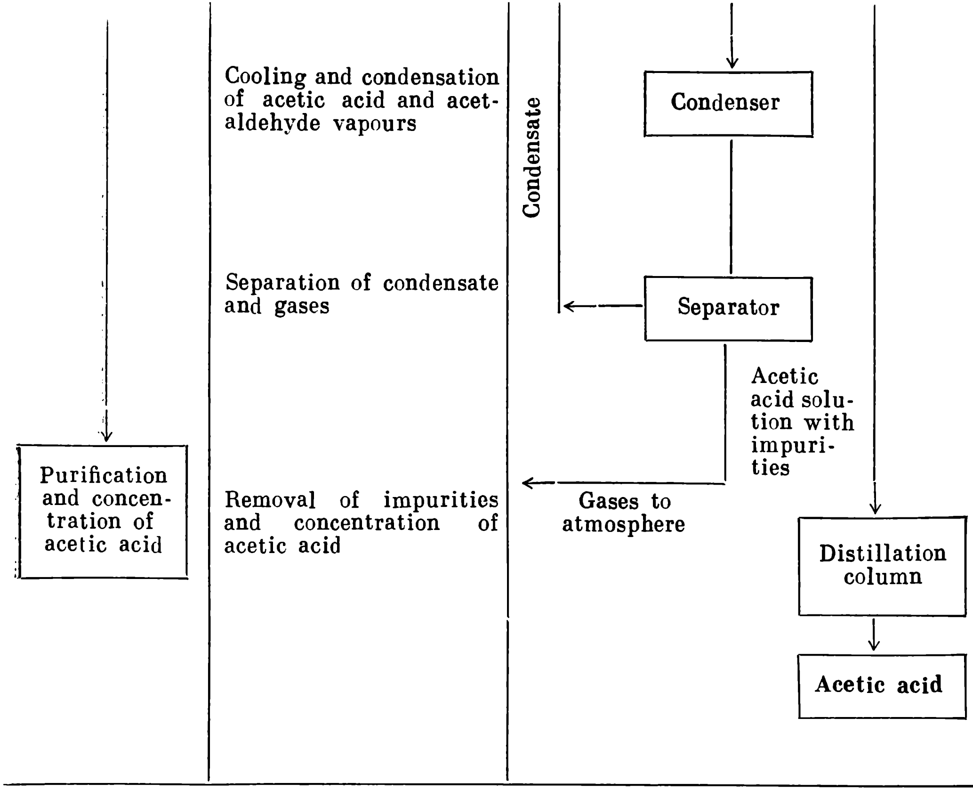


$$CH_3-C(=O)H + O_2 \rightarrow CH_3-C(=O)-O-OH + Q \qquad (14.9)$$

peracetic acid

TABLE 25. **Manufacture of Acetic Acid**

Process	Operation	Apparatus employed
Preparation of starting reactants	Preparation of acetaldehyde solution in acetic acid	 Acetaldehyde Mixer Acetic acid Oxygen Catalyst Mixer Oxidation column Vapours of acetic acid and acetaldehyde
↓	Preparation of catalyst solution in acetic acid	
Preparation of acetic acid	Oxidation of acetaldehyde  $2CH_3-C\overset{O}{\underset{H}{<}}+O_2\rightarrow 2CH_3C\overset{O}{\underset{OH}{<}}$	

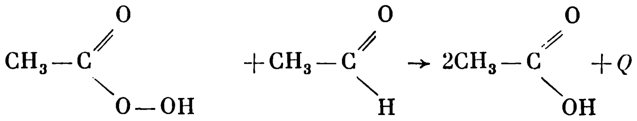

Purification and concentration of acetic acid
Condensate
Condenser
Separator
Acetic acid solution with impurities
Gases to atmosphere
Distillation column
Acetic acid

Cooling and condensation of acetic acid and acetaldehyde vapours

Separation of condensate and gases

Removal of impurities and concentration of acetic acid

Being a strong oxidizer, the peracetic acid reacts with acetaldehyde, converting it to acetic acid:



$$CH_3-C(=O)-O-OH + CH_3-C(=O)-H \rightarrow 2CH_3-C(=O)-OH + Q \qquad (14.10)$$

Both reactions evolve heat. To avoid accumulation of the peracetic acid which is capable of being decomposed explosively into elemental oxygen and acetic acid the process should be conducted so that peracetic acid is not accumulated in the reaction mixture, and it is converted to acetic acid as rapidly as possible. In order to do this, the oxidation process is generally carried out using a dilute solution of acetaldehyde in acetic acid, rather than pure acetaldehyde. Besides, converting peracetic acid to acetic acid may be accelerated by using a catalyst, such as a solution of manganese acetate $Mn(CH_3COO)_2$ in acetic acid.

Acetaldehyde is oxidized in the liquid phase at 60 to 70 °C. The schematic diagram for manufacturing acetic acid by liquid phase oxidation of acetaldehyde is shown in Fig. 92 and Table 25.

The basic apparatus is bubble-type oxidation column *2*. Acetaldehyde and catalyst solutions in acetic acid are introduced into this column. The solutions are prepared in mixers *1*. Air (or oxygen) is introduced into the column in concurrent flow with the liquid being oxidized. To remove the heat of the exothermic oxidation reaction and to maintain the desired temperature, the column is provided with cooling water coiled pipes along which water flows (not shown in the figure). It is very important to control thoroughly the temperature. If the temperature decreases below 60-70 °C, peracetic acid accumulates, and if the temperature rises side reactions become more intense.

The gases leaving oxidation column *2* contain vapours of acetic acid and acetaldehyde which are condensed in condenser *3* and cooled by a brine. After separator *4*, the condensate is returned to column *2*, and the gases are discharged to the atmosphere. The acetic acid which is removed from the column is split into two streams: the smaller is used to prepare acetaldehyde and catalyst solutions, and the larger is subjected to fractionation to remove impurities from the acetic acid and to increase its concentration. Fractionation is repeated twice to obtain a 97.5-98.5% acetic acid solution.

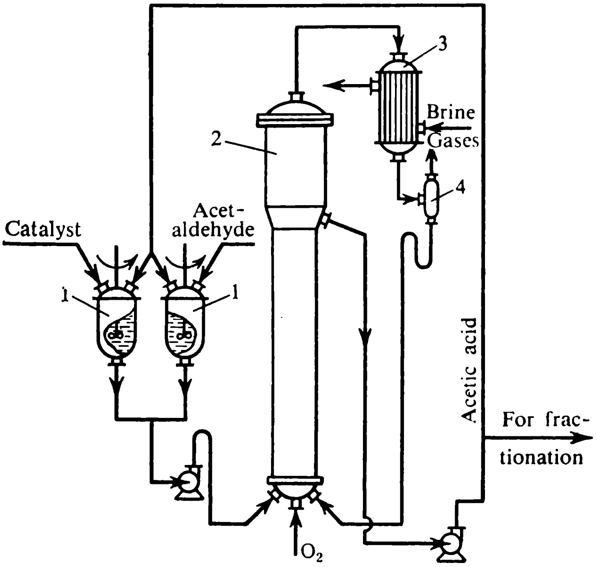
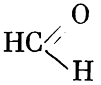


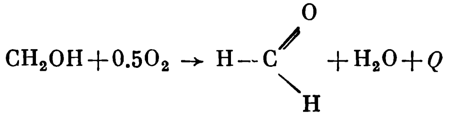
Fig. 92. Diagram for manufacturing acetic acid
1—mixers; *2*—oxidation column; *3*—condenser; *4*—separator

The Manufacture of Formaldehyde. Another important industry based on the catalytic oxidation process is the manufacture of a valuable product, formaldehyde.

At ordinary temperature formaldehyde  $\mathrm{HC}\genfrac{}{}{0pt}{}{\nearrow\!\!\!\nearrow \mathrm{O}}{\searrow \mathrm{H}}$ or formic aldehyde is a gaseous product with a sharp specific odour. Its boiling point is —21 °C and melting point is —92 °C. Aqueous formaldehyde solutions containing 33 to 40 per cent of formaldehyde are called formalin. Formaldehyde is highly reactive, that is why it came to be widely used as a raw material for synthesizing many organic compounds, such as synthetic resins and plastics, urothropine, and glycolic acid. Formaldehyde is a poison. Its aqueous solution—

formalin—is used as a seed treater, for the disinfection of vegetable storages and hotbeds.

To obtain formaldehyde, methanol is subjected to catalytic oxidation:



$$CH_2OH + 0.5O_2 \rightarrow H{-}C\begin{smallmatrix}{/\!\!/}O\\ \backslash H\end{smallmatrix} + H_2O + Q \qquad (14.11)$$

Methanol vapours are oxidized with atmospheric oxygen at temperatures of 500 to 700 °C with a catalyst such as silver applied onto pumice stone.

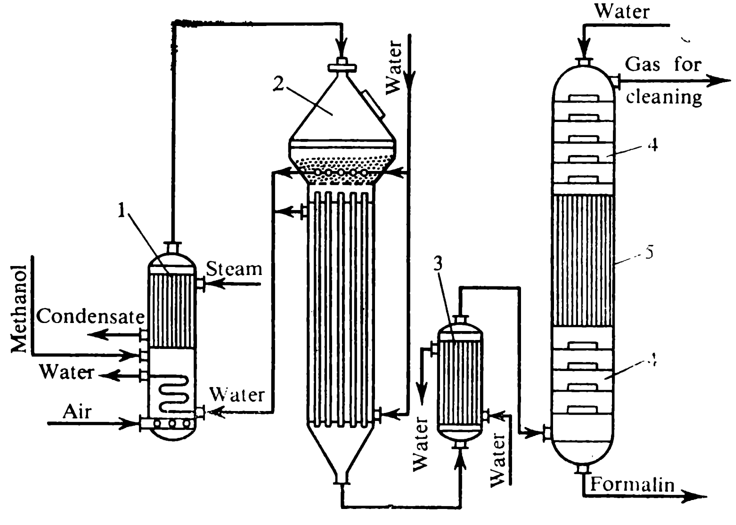
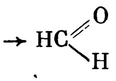


Fig. 93. Diagram for manufacturing formaldehyde
1—evaporator and superheater of alcohol; *2*—catalytic reactor; *3*, *5*—coolers; *4*—plate absorber

The diagram for formaldehyde manufacture using methanol oxidation is shown in Fig. 93 and Table 26. Methanol is admitted to the bottom of apparatus *1*—an alcohol evaporator. Air, essential for the oxidation process, is fed to the same apparatus. The air bubbles through a methanol layer. A temperature in the range of 40 to 50 °C is maintained in the alcohol evaporator by using hot water flowing in the

TABLE 26. **Manufacture of Formaldehyde**

Process	Operation	Apparatus employed
		Methanol ↓
Preparation of raw materials ↓	Heating of methanol and preparation of alcohol—air mixture	Air → Alcohol evaporator ↓
	Heating of alcohol-air mixture	Alcohol superheater ↓
Preparation of formaldehyde ↓	$CH_3OH + 0.5O_2 \rightarrow$  $\rightarrow HC\begin{smallmatrix}{=}O\\ H\end{smallmatrix}$	Catalytic apparatus ↓
	Cooling of gas mixture	Cooler ↓
Separation of formaldehyde	Absorption of formaldehyde with water	Water → Absorber → Gases ↓
		Formaldehyde solution (formalin)

coiled pipes. The methanol evaporates and forms an alcohol-air mixture together with the air bubbling through it. The mixture is admitted to the top of apparatus *1*—an alcohol superheater—in which the former is heated to 110 °C. The mixture heated to such a temperature flows into catalytic reactor *2* where formaldehyde is formed in a silver catalyst bed at temperatures of 650 to 700 °C.

The oxidation process is carried out autothermically. The temperature condition in the catalyst bed is controlled by varying the amount and temperature of the alcohol-air mixture fed into the apparatus, and of water fed into the tubes located in the bed.

Below the catalyst bed, the catalytic reactor is a cooler in which the hot contact gas passes through the pipes being cooled with water. This water is then used at the bottom of apparatus *1* (alcohol evaporator) to attain the temperature needed to evaporate the methanol. The gas leaving catalytic reactor *2* contains not only formaldehyde, but also nitrogen and impurities, such as CO_2, CO, CH_4, CH_3OH. Therefore, gas having a temperature of 60 °C, passing through another cooler *3* where it is cooled with water, flows into absorption tower (tray absorber) *4* in which the formaldehyde is absorbed with water. To remove heat, the absorption column *4* is provided with internal cooler *5*. The final product, 33-40 per cent aqueous formaldehyde (formalin), is removed from the bottom of column *4*. The solution contains 10 to 12 per cent of methanol. This impurity is desirable since it prevents formaldehyde from polymerizing during storage.

14.6 The Halogenation of Hydrocarbons

Among the various halogenation processes, chlorination of hydrocarbons has found wide application. The valuable properties of the resulting products and the availability of elemental chlorine required to produce them have contributed to developing the manufacture of organochloric compounds.

Chlorine in hydrocarbons may substitute the hydrogen atoms or be added at the position of the unsaturated bonds between the carbon atoms. Not only chlorine but also chlo-

TABLE 27. **Manufacture of Vinyl Chloride**

Process	Operation	Apparatus employed
		Hydrogen chloride ↓ Acetylene ↓
Preparation of raw materials ↓	Mixing of starting reactants	Mixer ↓
Preparation of vinyl chloride ↓	$CH{\equiv}CH + HCl \rightarrow CH_2{=}CHCl$	Tubular catalytic reactor ↓
Recovery of vinyl chloride ↓	Water washing to remove HCl	Water → Scrubber → ↓
	Neutralization of hydrochloric acid	Alkali solution → Scrubber → ↓
	Desiccation with solid alkali	Desiccator ↓
	Cooling of gases and condensation of vinyl chloride	Cooler-condenser ↓
Cleaning of vinyl chloride	Removal of impurities from vinyl chloride	Distillation column ↓
		Vinyl chloride

rine-containing compounds may be used for chlorination purposes.

Hydrocarbons chlorination using hydrogen chloride—so-called **hydrochlorination**—has great practical importance. Chlorination of hydrocarbons is effected in the vapour and liquid phases by various methods, i.e. by heating (thermal chlorination), in the presence of catalysts (catalytic chlorination), and by special illumination of the reacting components (photochemical chlorination).

Vinyl chloride $CH_2{=}CHCl$ is a very important raw material for producing polymers which are essential in the manufacture of plastics and synthetic fibres. Vinylchloride can be obtained by hydrochlorination of acetylene:

$$CH{\equiv}CH + HCl \rightarrow \underset{\substack{\text{vinyl}\\ \text{chloride}}}{CH_2{=}CHCl} \tag{14.12}$$

Industrial hydrochlorination of acetylene is effected in the liquid or gaseous phase. The latter method is more promising, since simpler equipment is required for carrying it out, and the process may be easily automated.

Hydrochlorination of acetylene takes place at 170 °C in the gaseous phase (Fig. 94 and Table 27). A mixture of hydrogen chloride and acetylene flows from mixer *1* into tubular catalytic reactor *2* whose tubes are filled with a catalyst, mercury chloride, applied to activated carbon. The reaction heat is removed with a cold mineral oil that circulates in the intertube space of the reactor. The gases leaving catalytic reactor *2* and containing 93 per cent of vinyl chloride and 5 per cent of hydrogen chloride are admitted to scrubbers *3* where they are first washed with water to remove the hydrogen chloride and then neutralized with alkali. In apparatus *4*, the vinyl chloride is desiccated with solid alkali. The vinyl chloride is then condensed in condenser *5* being cooled with a brine, and then subjected to fractionation to remove impurities.

Chlorination of aromatic compounds has been widely employed. Benzene chlorination in the presence of a catalyst produces *chlorobenzene* which is used as a semi-product in the manufacture of synthetic dyes, phenol, insecticide ДДТ, and as a solvent of some esters of cellulose and other polymers.

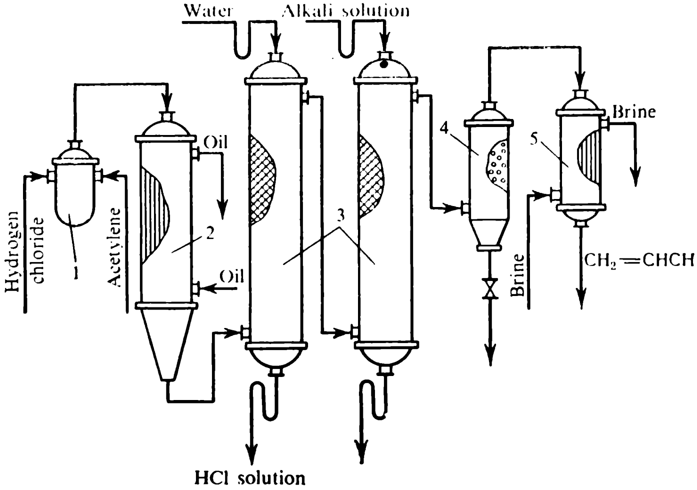


Fig. 94. Diagram for manufacturing vinyl chloride
1—mixer; 2—catalytic reactor; 3—scrubbers; 4—drying apparatus; 5—condenser

Fluorochlorosubstituted hydrocarbons of the saturated and unsaturated series are used to manufacture plastics, such as fluoroplastics. Chloroform reacts with hydrogen fluoride to form difluorochloromethane:

$$CHCl_3 + 2HF \rightarrow CHF_2Cl + 2HCl \qquad (14.13)$$

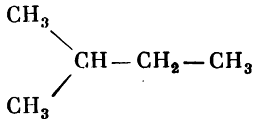
Pyrolysis of difluorochloromethane at 650 °C in the absence of a catalyst produces tetrafluoroethylene from which fluoroplastic-4 (teflon) is obtained:

$$2CHF_2Cl \xrightarrow[650\ ^\circ C]{\text{pyrolysis}} CF_2{=}CF_2 + 2HCl \qquad (14.14)$$

14.7 Other Methods for Manufacturing the Products of Basic Organic Synthesis

Along with the methods previously described, organic synthesis widely employs some other methods, such as isomerization, alkylation, sulphonation, and nitration of hydrocarbons.

Isomerization changes the structure of hydrocarbon molecules without changing their molecular weight and composition. This method yields branched chain hydrocarbons which can be used, for example, to improve antiknock stability of motor fuels. Isopentane



is produced in the isomerization of *n*-pentane CH_3—$(CH_2)_3$——CH_3 and has an octane number of 105.7, whereas *n*-pentane has an octane number of 88.7.

Alkylation adds an alkyl group to the molecule of an organic compound. Alkylation of fatty hydrocarbons reacts olefins with *iso*-paraffin. Alkylation of fatty hydrocarbons yields high-octane additives to motor fuels.

Sulphonation is the substitution of the sulphonic group SO_3H for the hydrogen atoms of the starting hydrocarbons. It is effected using oleum, concentrated sulphuric acid, more rarely sulphur trioxide, bisulphates, and bisulphites. Sulphonation is employed to manufacture major products, such as benzene sulphonic acid and phenol.

Nitration substitutes the nitro group NO_2 for the hydrogen atoms in the hydrocarbon and is employed to manufacture nitrobenzene.

REVIEW QUESTIONS

1. What is the significance of basic organic synthesis for the chemical industry?
2. Name the major industrial products of basic organic synthesis?
3. What types of raw materials are used in the organic synthesis industry?
4. Name the major types of reactions that are most frequently employed in the basic organic synthesis industry.
5. Name the industries where a method of the dehydrogenation of hydrocarbons is employed.
6. What is the manufacture of butadiene based on according to S. Lebedev?

7. What is methanol used for?
8. What conditions are essential for successful synthesis of methanol?
9. What are the common features in the processes for manufacturing ammonia and methanol?
10. What can be done to suppress the side reactions in the synthesis of methanol?
11. What methods can be used for producing ethanol from ethylene?
12. What basic industries is ethanol used for?
13. Name the industries based on oxidation reactions.
14. Write the reactions that produce acetic acid from acetaldehyde.
15. What is acetic acid used for?
16. How is formaldehyde produced and where is it used?
17. Name some products that can be obtained by the hydrocarbon halogenation method.

Chapter 15

HIGH-MOLECULAR COMPOUNDS

15.1 General Information on High-molecular Compounds

The whole of nature, both living and non-living, is made up of molecules which, in turn, are composed of atoms. Being joined to each other in varying ratios, atoms form molecules that differ by their size, structure, chemical composition, and properties.

Substances made up of a small number of atoms are called **low-molecular**. Their molecular weight does not exceed several hundreds of units. Salts, acids, alkalis, alcohols, and other compounds are low-molecular substances.

At the same time, many substances are made up of giant molecules which incorporate thousands, tens, and hundreds of thousands of atoms. Such molecules are known as **macromolecules**; their molecular weight is hundreds and thousands of units. For example, the molecular weights of the molecules that compose natural rubber are 136 000 to 340 000.

Compounds made up of macromolecules are called **high-molecular** or **polymers**.

By their origin, polymers are subdivided into natural and synthetic.

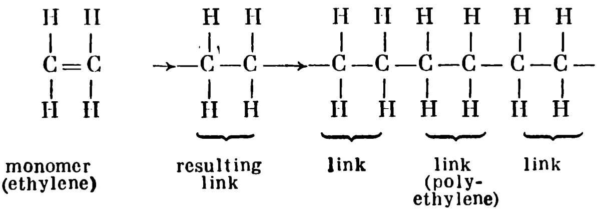
Natural, i.e. naturally occurring, polymers include cellulose which is part of wood, cotton, and other plants; proteins which are part of living organisms; natural rubber, etc.

Synthetic polymers can be obtained artificially by chemical synthesis. They are incorporated into the composition of plastics, synthetic rubbers, chemical fibres, and varnishes.

The Composition and Properties of Polymers. Polymer molecules are long chains with similar alternating links. If these links are designated as A, the polymer molecule may be represented as follows:

$$-\mathrm{A}-\mathrm{A}-\mathrm{A}-\mathrm{A}-\mathrm{A}-\mathrm{A}- \qquad (15.1)$$

In synthetic polymers, these links are residues of the molecules of original compounds composed of just a few atoms. These original compounds are called **monomers**. For example, ethylene, $\mathrm{CH_2CH_2}$, is a monomer used to prepare a high-molecular compound called polyethylene. When a polymer is formed, the double bond between the carbon atoms opens in the ethylene molecules. Then due to free carbon valences being formed, a great number of the links resulting from the monomer are joined together. Schematically, this may be represented as follows:



$$\underset{\substack{\text{monomer}\\ \text{(ethylene)}}}{\overset{\mathrm{H}\ \ \mathrm{H}}{\underset{\mathrm{H}\ \ \mathrm{H}}{\mathrm{C{=}C}}}} \quad \rightarrow \underbrace{-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}}_{\substack{\text{resulting}\\ \text{link}}} \longrightarrow \underbrace{-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}}_{\text{link}} \underbrace{-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}}_{\substack{\text{link}\\ \text{(poly-}\\ \text{ethylene)}}} \underbrace{-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{C}}}-}_{\text{link}} \qquad (15.2)$$

The diagram shows only three links in the polymer composition; in actual fact, their number in polyethylene varies from 1000 to 10 000, and the molecular weight of such a polymer varies from 28 000 to 280 000.

It can be seen from the diagram that both the monomer and the polymer have one carbon atom and two hydrogen atoms, i.e. the elemental composition of the polymer is identical to that of the monomer.

Changing the number of interlinked monomer molecules changes the properties of the polymers obtained. For example, as the molecular weight increases, polyethylene becomes more viscous, then pasty, and finally solid. The properties of the polymers also depend on the chemical composition of the monomers, the shape of molecule chains and their structure (the polymer structure).

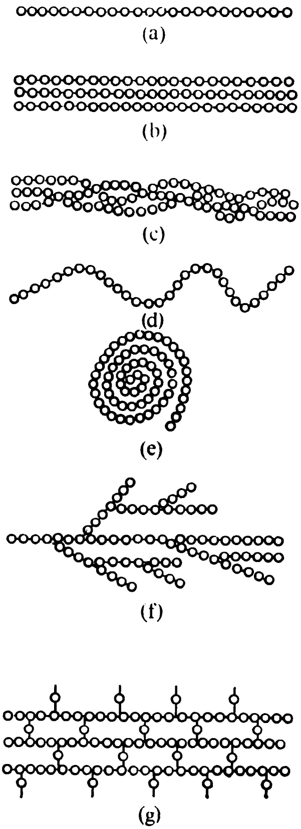


Fig. 95. Structures of macromolecules

In a linear macromolecule these elementary links form a thread-like molecule, i.e. each link is joined to only two neighbouring ones (Fig. 95*a*). Thread-like (linear) macromolecules may be arranged in a polymer in parallel to each other (Fig. 95*b*) or intertwined without the chemical bond of individual macromolecules (Fig. 95*c*). They may be curved or rolled into balls (Fig. 95*d* and *e*). Linear macromolecules can be found in polyethylene, polypropylene, cellulose, polyesters, polyamides, and many other high-molecular compounds. They are widely used to manufacture fibres, films, plastics, and rubber. These polymeric materials are generally strong, elastic, and can be dissolved or fused by heating.

Branched-chain macromolecules have side branches off the main chain (Fig. 95*f*). Polymers having branched-chain molecules dissolve or fuse less readily than linear polymers.

The structure of **cross-linked** macromolecules is as follows: the long chains of molecules are interlinked by short chains in three dimensions; this is difficult to depict in the figure. This polymer molecule structure is generally shown in the form of large interlinked linear macromolecules (Fig. 95*g*). In this case, it should always be kept in mind that linear molecules are chemically bonded with molecules arranged above the plane and beyond the plane of paper. This molecular structure is also known as **spatial** or **three-dimensional**. The greater the number of "bridges" in such a macromolecule, the less elastic the polymer is, and it exhibits, to a considerable measure, the properties of a solid.

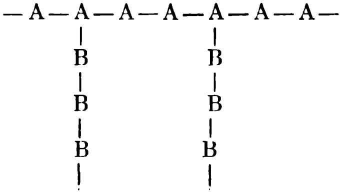
The chain structure of polymeric molecules may be different. In some cases, polymeric molecules are formed, whose elementary links have a different spatial arrangement of the side groups. In other cases, the elementary links have a strictly spatial arrangement. Polymers having a strictly regular structure of molecules are called **isotactic**. These polymers are very hard and thermally stable.

Polymer molecules may be made up of unsimilar links, as shown in Eq. (15.1). They can be formed from different monomers, for example A and B. The macromolecule can then be presented as follows:

$$-A-B-A-B-A-B-A-B-A-B \tag{15.3}$$

These high-molecular compounds are called **copolymers**. They combine the typical properties of polymers derived from each component individually. Thus, specific properties may be imparted to polymers, i.e. to obtain rubbers having improved petrol- and oil-resistance, chemical stability, etc.

So-called **graft copolymers** are of certain interest. The chain structure of their molecules can be presented as follows:



$$\begin{array}{ccccccccccccccc} - & A & - & A & - & A & - & A & - & A & - & A & - & A & - \\ & & & | & & & & & & | & & & & & \\ & & & B & & & & & & B & & & & & \\ & & & | & & & & & & | & & & & & \\ & & & B & & & & & & B & & & & & \\ & & & | & & & & & & | & & & & & \\ & & & B & & & & & & B & & & & & \\ & & & | & & & & & & | & & & & & \end{array} \tag{15.4}$$

This polymer is like a fruit tree to which another kind of a fruit tree is grafted. Such "grafting" yields fruits combining the most valuable qualities of both kinds. In the graft copolymer, one polymer is grafted to the "trunk" of the other polymer. The resulting hybride possesses the properties of the original substances. Thus, polymers can be obtained which combine, for example, high electric-insulating properties with fire-, petrol-, and oil resistance.

Macromolecules may be made up of "blocks" of relatively low molecular weight which are formed from various monomers. The structure of such a **block copolymer** can be presented as follows:

$$—A—A—A—A—B—B—B—A—A—A—A—B—B—B— \quad (15.5)$$

Block copolymers also combine the properties of the original polymers.

The elementary links in macromolecules have, so far, been conventionally designated as A and B. It can be seen from Eq. (15.2) that the organic polymers are based on carbon atoms which are joined together to form a molecular "skeleton" framed by hydrogen atoms. Instead of hydrogen atoms, there may be groups of atoms which, in addition to carbon atoms, contain atoms of other elements.

If the skeleton of the polymer molecules is made up of carbon atoms, they are called **carbon-chain** polymers. There are molecules having carbon atoms periodically alternated in the skeleton with atoms of other elements, for example:

$$—N—C—C—C—C—C—C—C—N—C—C—C—C—C—C—C—N— \quad (15.6)$$

Such polymers are called **hetero-chain** polymers.

The behaviour of polymers when heated depends on the structure of molecules. During heating, linear and branched polymers become soft and, when cooled, are transformed into the solid state. Such polymers are called **thermoplastic** polymers. Polymers that have a spatial structure and do not melt when heated are called **thermosetting** polymers.

The transition temperature of a polymer from the solid to the elastic state (or vice versa) is called the **vitrification temperature**, and the transition temperature to the flow state, the **flow temperature**.

Polymers may be either completely amorphous substances, **amorphous polymers**, or substances containing crystalline and amorphous regions, **crystalline polymers**. Polymers are subdivided into **solid polymers**, **elastic polymers** or **elastomers**, and **flow polymers** according to the strains that develop in polymers due to the effect of external conditions at room temperature.

Thus, by varying the size of the resulting molecule, its molecular weight and shape, making the macromolecule from various initial monomers, grafting to the macromolecule a polymer chain made up of links formed by the other monomer, it is possible to change the physical and chemical properties of polymers within wide ranges, obtain polymers having predetermined properties, change their physical state, and make them liquid, solid, plastic, and elastic.

Polymers possess low density (the lightest plastics are 800 times lighter than steel), high mechanical strength (it exceeds the strength of wood, glass, and ceramics), high thermal-, sound- and electric-insulating properties, high chemical stability, and fine optical properties. They can absorb and suppress vibrations, form exceedingly thin films and fibres. They can be readily processed into manufacture articles.

The valuable properties of polymers caused their wide applications in various industries of the national economy, such as machine-building, construction, automobile, aviation, atomic, cosmic industries and other fields of engineering, in the manufacture of fabrics, artificial leather, domestic appliances and in medicine.

15.2 Methods of Synthesis of Polymers

Polymers can be obtained by polymerization or polycondensation methods.

Polymerization. The polymerization process joins together the monomer molecules into large molecules using heat, catalysts, γ-rays, light, and initiators. Linear, branched, cross-linked molecules, molecules of copolymers, graft copolymers are formed in this way.

The polymerization rate and the molecular weight of the polymer depend on temperature, pressure, catalyst activity, etc.

There exist the following polymerization methods: bulk polymerization (bulk method), emulsion polymerization, solution polymerization, and suspension polymerization.

Bulk polymerization occurs in an apparatus (autoclave) where the initial monomer is fed together with a catalyst or an initiator, i.e. a substance that reacts with the monomer and accelerates polymerization. As the polymerization process begins, the reacting mass is preheated, then the preheating is discontinued since the polymerization process evolves heat. To maintain a certain temperature in the apparatus, the reacting mass is sometimes cooled during the polymerization. When polymerization is completed, a solid mass of polymer in the form of a block is extracted from the apparatus. The polymerization process may be either batch or continuous. In bulk polymerization, it is difficult to secure the same temperature in the whole reacting mass, therefore the resulting polymer consists of macromolecules having different degrees of polymerization. This method is used to manufacture polystyrene, polymers of methacrylic acid, and butadiene rubber.

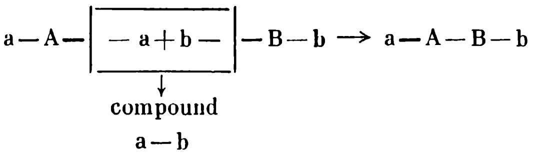
In the *emulsion polymerization process* a monomer is mixed with an initiator and an emulsifier, and is transformed by agitators into fine droplets suspended in the other liquid, most frequently in water. (Emulsifiers are substances that prevent adhesion of liquid droplets.) The resulting emulsions are heated to a temperature at which polymerization occurs. In this case, the heat liberated during the polymerization process is easily removed, and the resulting polymer is more homogeneous than that obtained by the block method. The process is disadvantageous in that it is difficult to separate the emulsifier from the polymer. This process is used to obtain copolymers of butadiene, vinyl acetate, and acrylonitrile.

Solution polymerization occurs in a solvent which is miscible with a monomer and can dissolve the resulting polymer. The polymer is recovered from the resulting solution by evaporating the solvent or by precipitation. The polymerization process is also carried out in a solvent that dissolves the monomer, but does not dissolve the polymer. In this case, the polymer precipitates and is then filtered.

This process is used to obtain polyvinyl acetate, polybutylacrylate, and other polymers.

The *suspension polymerization process* grinds (disperses) the monomer into droplets in a poorly dissolving medium, generally in water. The polymerization process occurs in each monomer droplet. Water-insoluble particles of the resulting polymer precipitate and are separated from the liquid by filtration.

Polycondensation. The method resides in that monomer molecules are joined together and then reacted to precipitate side products. For example, let us designate the molecule of one of the reactants as a—A—a, and the second molecule, b—B—b. The diagram of the reaction between them is as follows:



$$a-A-\underset{\substack{\downarrow\\ \text{compound}\\ a-b}}{\boxed{-a+b-}}-B-b \longrightarrow a-A-B-b \qquad (15.7)$$

As can be seen from Eq. (15.7), a molecule of the compound a—A—B—b was formed from the reacting molecules, and compound a—b separated. The molecule of the compound a—A—B—b may further be reacted with monomers. By adding new monomer molecules, the polymer chain grows longer. Here, the addition of each new molecule is accompanied by the separation of the compound a—b. As a result, the polymer molecules differ somewhat from the initial monomers in chemical composition.

The polycondensation process yields both linear and cross-linked polymers.

The polycondensation process is exothermic and therefore, according to the Le Chatelier principle, it is necessary to carry out the process at low temperatures to shift the equilibrium from the left to the right. However, to increase the process rate, the temperatures should be raised. Therefore, to increase the polycondensation rate, the process is first carried out at elevated temperatures which are then gradually lowered to shift the reaction equilibrium, thus yielding a higher molecular weight product.

Polycondensation is effected both with or without a catalyst. It is carried out in a melt, solution or at the phase interface.

Melt polycondensation is effected at high temperatures of 220 to 280 °C in a reactor in an inert gas atmosphere, which ensures a high rate for the process and removes low-molecular products.

During solution polycondensation monomers are dissolved in solvents—the reaction occurs at a low rate, and the low-molecular products are not completely removed. This process has not found industrial application.

Interfacial polycondensation is accomplished with two immiscible liquids each of which contains dissolved initial monomers. The polycondensation reaction occurs instantaneously at the phase interface to form a film of polymers. The reaction products are then withdrawn from the reaction. This promotes a high reaction rate. As the film is removed, the interface becomes clear, and the reaction continues.

REVIEW QUESTIONS

1. What compounds are called high-molecular weight compounds?
2. Draw linear, branched, and cross-linked molecules. What are their properties?
3. Draw diagrammatically molecules of various types of copolymers.
4. What are carbon-chain and hetero-chain polymers?
5. What methods for polymer synthesis do you know?
6. What are the essential points of bulk, emulsion, solution, and suspension polymerization?
7. What polycondensation processes do you know?
8. How do thermoplastic polymers differ from thermosetting ones?

Chapter 16

THE TECHNOLOGY OF PLASTICS

Plastics are a group of materials that consist completely or partially of polymers, and possess plasticity at some processing stage.

Plasticity is the ability of a body for plastic strain which changes the shape of the body under the effect of external mechanical forces without disturbing the bond between particles. In this case, a new shape is retained after external loads are no longer applied.

Plastics possess a great variety of properties. The mechanical strength of individual types of plastics exceeds the strength of wood, metal and ceramics, and at the same time they are much lighter than these materials. Plastics are not only solid, but also elastic like rubber. They feature high dielectric properties and can be processed into final products of the most various and complicated shapes without any difficulty. They can also be readily moulded, cast, ground, polished, and elongated into filaments or films.

These remarkable qualities of plastics made it possible for them to be employed on a very wide scale for the manufacture of machine components, instruments, aircraft, automobiles, vans, ships, and so on. They are also used in medicine, for every day use, and in agriculture. It is difficult to name any branch of the national economy which would not employ plastics.

However, plastics have low thermal stability and are liable to "ageing". Most plastics are serviceable at temperatures up to 150 °C, and some up to 300 °C. As plastics age the composition and structure of macromolecules undergo changes due to various factors, such as oxidation and radiation.

Some plastics are comprised only of polymers. They are called **simple plastics**. Others are essentially a composition which includes, in addition to polymers, fillers, plasticizers, dyes, hardeners, and stabilizers. These are called **filled plastics**. Any plastic is based on high-molecular polymeric compounds which bind together all the components of the composition. These polymers are called **binding.**

Fillers are non-plastic compounds. These may be finely divided solid materials: wood meal, gypsum, kaolin, soot, graphite, or talc; fibrous fillers, such as cotton, textile waste, asbestos fibre, paper, cotton cloth, or glass fibre. Fillers improve the mechanical and chemical properties of plastics. For example, they improve their thermal stability, strength, incombustibility, water resistance, electric-insulating properties, and external appearance. Since fillers are cheap compounds, their addition to the composition cuts down the cost of the finished articles.

Plasticizers are compounds, mostly liquids, which when added make it easier for the mixture to be transformed into the plastic state and, hence, improve the process of moulding articles from plastics. Camphor, castor oil, dibutyl phthalate, and other compounds are used as plasticizers.

Dyes are added to the mixture to give a certain colour to articles.

Hardeners are added to change the structure of polymers, i.e. to transform linear molecules into spatial ones and thus to prepare an insoluble and solid mass.

Stabilizers are compounds that preserve the initial properties of polymers and prevent the change in their properties with time.

Depending on their chemical structure and the method of polymer synthesis, plastics are subdivided into four groups.

1. Plastics based on high-molecular compounds produced by chain polymerization. These are plastics based on polymers of ethylene, vinyl alcohol and their derivatives.
2. Plastics based on high-molecular compounds produced by polycondensation. These are plastics based on phenol aldehyde (phenoplasts), amine-formaldehyde resins (aminoplasts), etc.
3. Plastics containing natural polymers. These are ethers and esters of cellulose (celluloid, etrols) and proteins (gallalite).
4. Plastics based on natural and petroleum asphalts and also on resins.

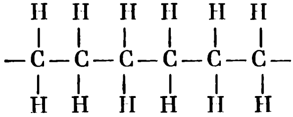
Besides, mixed type plastics are manufactured industrially which contain resins of various classes, thus producing materials having a great variety of properties.

Depending on the type of polymers that are part of the plastics, there are thermoplastics (thermoplasts) and thermosetting plastics. The difference between them has been dealt with above.

16.1 Polymerization Resin-based Plastics

Polymerization resins, such as polyethylene, polystyrene, polyvinyl chloride, and polymethyl methacrylate, are thermoplasts.

The Manufacture of Polyethylene. The manufacture of one of the most widely used types of polymerization plastics is based on the polymerization reaction of a gaseous product, ethylene $H_2C{=}CH_2$. This reaction yields the compound:



$$\begin{array}{ccccccccccccc} & H & & H & & H & & H & & H & & H & \\ & | & & | & & | & & | & & | & & | & \\ - & C & - & C & - & C & - & C & - & C & - & C & - \\ & | & & | & & | & & | & & | & & | & \\ & H & & H & & H & & H & & H & & H & \end{array}$$

The polyethylene chain consists of a great number of $—CH_2—CH_2—$ links. Therefore, the formula of polyethylene may be written as follows: $(—CH_2—CH_2—)_n$.

Ethylene polymerization is carried out at high, mean or low pressures. Ethylene polymerization is conducted at a *high pressure* of 1000 to 3000 kgf/cm^2, more frequently at 1500 kgf/cm^2, at a temperature of 220 to 280 °C, and in the presence of small amounts of oxygen. This process is carried out in plants whose schematic diagram is depicted in Fig. 96 and Table 28. Purified gaseous ethylene with the addition of a small amount of oxygen (catalyst) is compressed together with the unreacted ethylene in compressor *1* to 1500 kgf/cm^2. From the compressor the ethylene is directed to oil separator *2* where it is purified of the lubricating oil that gets into the compressed ethylene in the compressor. The ethylene is then admitted to reactor *3* where it undergoes polymerization. The temperature is maintained at about 100 °C at the top of the reactor and about 200 °C, at the bottom.

The reactor is a system of inclined thick-wall pipes with an internal diameter of up to 25 mm and a length of 300 m.

The degree of polymerization (the degree of conversion) of ethylene per one pass through the reactor varies from 10 to 12 per cent. After reactor *3* the resulting polyethylene and the unreacted ethylene pass through separator *4* where

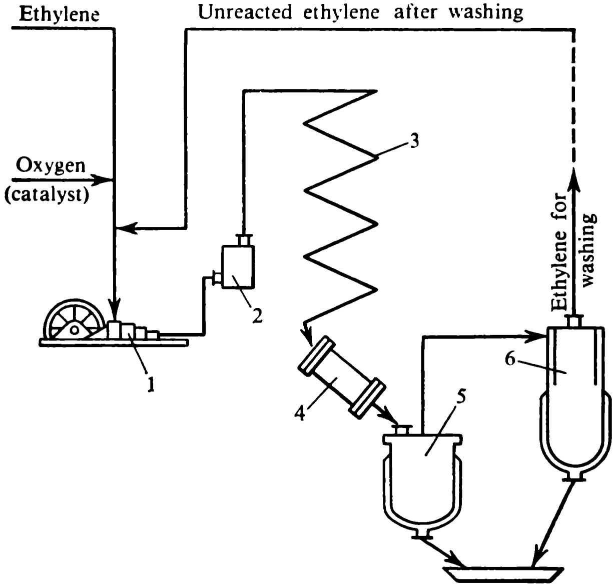


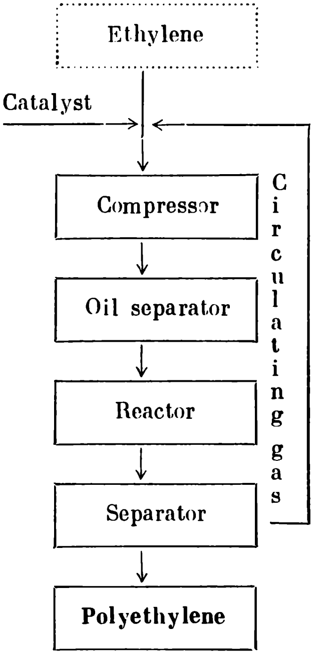
Fig. 96. Diagram for manufacturing polyethylene
1—compressor; *2*—oil separator; *3*—reactor; *4*—separator; *5*—receiver; *6*—trap

the polyethylene is separated and collected in receiver *5*. After the pressure is reduced, the unreacted ethylene is separated from the polyethylene and sent through trap *6* to be washed and is then fed to compressor *1*. During repeated circulation of the ethylene, its degree of conversion to polyethylene is 95 to 97 per cent. So, in this case a cyclic flow diagram is employed. From receiver *5* and trap *6*, the polyethylene is stabilized and, if desired, tinted, granulated and then processed into articles.

High-pressure polyethylene has low density.

Ethylene polymerization is carried out at a *mean pressure* of 30 to 70 kgf/cm^2 in the presence of a catalyst (Cr_2O_3, CrO_3,

TABLE 28. **The Manufacture of Polyethylene**

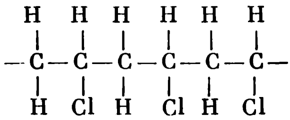
Process	Operation	Apparatus employed
Preparation of gas ↓	Compression of ethylene Removal of lubricating oil	 Ethylene Catalyst Compressor Oil separator Reactor Separator Polyethylene Circulating gas
Polymerization of ethylene ↓	$n\,(H_2C{=}CH_2) \to$ $\to(-CH_2-CH_2-)_n$	
Separation of polyethylene	Separation of polyethylene and circulating gas	

etc.). The ethylene is dissolved in petrol, and when contacted with the catalyst at a temperature of 110 to 140 °C ethylene polymerizes. On completion of the reaction, the polymer is separated from petrol, washed, dried and granulated.

Ethylene polymerization at a *low pressure* of 2 to 6 kgf/cm^2 as well as at mean pressure is effected in a solution, e.g. in petrol, at a temperature of 60 to 80 °C in the reactor and with a catalyst, a mixture of triethyl aluminium, $(C_2H_5)_3Al$, and titanium tetrachloride, $TiCl_4$. After separation from petrol, the polyethylene is washed with alcohol, dried, and granulated.

Polyethylene exhibits a high chemical stability and good dielectric properties. It is widely used to manufacture pipes, cocks, gears, storage battery tanks, cables, components of radio- and television sets and telegraph apparatus, dishware, films, synthetic fibres, and so on. It should be noted that polyethylene produced at low pressures is more resistant to organic acids and solvents, but less elastic. It is more difficult to be processed into articles than high-pressure polyethylene.

The Manufacture of Polyvinyl Chloride. Polyvinyl chloride is a polymer consisting of the elementary links $—CH_2—$ $—CHCl—$:



$$\begin{array}{cccccccccccc} & H & & H & & H & & H & & H & & H \\ & | & & | & & | & & | & & | & & | \\ — & C & — & C & — & C & — & C & — & C & — & C — \\ & | & & | & & | & & | & & | & & | \\ & H & & Cl & & H & & Cl & & H & & Cl \end{array}$$

Hence, the formula of polyvinyl chloride is: $(—CH_2—$ $—CHCl—)_n$.

Vinyl chloride $CH_2{=}CHCl$, which is a gas under ordinary conditions, serves as raw material for the manufacture of polyvinyl chloride.

Polymerization of vinyl chloride is generally carried out in an aqueous emulsion that is produced when the vinyl chloride is mixed with water at 35 to 70 °C and at 5 to 8 kgf/cm^2, in the presence of an emulsifier, gelatin, and an initiator, benzoyl peroxide. When the polymerization process is completed, the reaction mass is transferred to an apparatus to distill the unreacted vinyl chloride, which is then purified and returned for polymerization purposes. The resulting polyvinyl chloride is separated from water by centrifuging and dried.

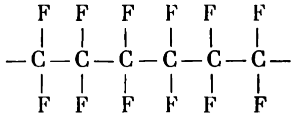
Polyvinyl chloride may be produced as a brittle solid substance—vinyl plastic or as an elastic material—plasticate.

Vinyl plastic is produced from pure resin with a stabilizer (amines and metal oxides). It has high strength, can be readily machined or welded, and is chemically stable. However, vinyl plastic is soluble in nitric acid and in aromatic and chlorinated hydrocarbons.

Plasticate is produced by mixing polyvinyl chloride with a plasticizer (phosphoric and phthalic anhydrides). It is used for lining and sealing chemical equipment, in the manufacture of leather substitutes, hoses, linoleum, oil cloths, conveyer belts, and domestic appliances.

The Manufacture of Fluoroplastics. Fluoroplastics are superior in their chemical stability to all the known materials, including gold and platinum. Fluoroplastics are produced by polymerization of tetrafluoroethylene $CF_2{=}CF_2$ or trifluorochloroethylene $CF_2{=}CFCl$.

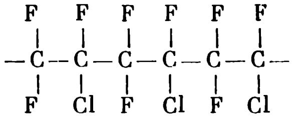
In the first case, the compound



$$-\underset{F}{\overset{F}{C}}-\underset{F}{\overset{F}{C}}-\underset{F}{\overset{F}{C}}-\underset{F}{\overset{F}{C}}-\underset{F}{\overset{F}{C}}-\underset{F}{\overset{F}{C}}-$$

is formed. It has the formula $(-CF_2-CF_2-)_n$ and is referred to as fluoroplastic-4.

Polymerization of trifluorochloroethylene yields the following compound:

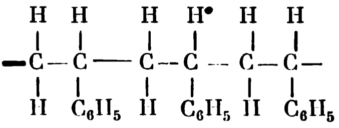


$$-\underset{F}{\overset{F}{C}}-\underset{Cl}{\overset{F}{C}}-\underset{F}{\overset{F}{C}}-\underset{Cl}{\overset{F}{C}}-\underset{F}{\overset{F}{C}}-\underset{Cl}{\overset{F}{C}}-$$

It has the formula $(-CF_2-CFCl-)_n$ and is referred to as fluoroplastic-3.

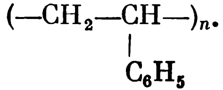
In addition to high chemical stability, fluoroplastics have good electroinsulating properties and withstand temperatures in the range of —190 to +200 °C. They can be temporarily used at temperatures even as high as 300 to 400°C. They are most valuable for the manufacture of apparatus components, gaskets, sheets, films, pipes, rods and other articles operating at elevated temperatures in a highly aggressive medium. However, it should be noted that it is difficult to process fluoroplastics into usable articles.

The Manufacture of Polystyrene. Polystyrene is produced from styrene, $CH_2{=}CH-C_6H_5$ (phenylethylene). Polymerization yields the following compound:



$$-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{C_6H_5}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{C_6H_5}}{\overset{\mathrm{H^\bullet}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{C_6H_5}}{\overset{\mathrm{H}}{\mathrm{C}}}-$$

It has the formula



$$(-\mathrm{CH_2}-\underset{\mathrm{C_6H_5}}{\underset{|}{\mathrm{CH}}}-)_n.$$

Polymerization is carried out by varnish, emulsion, and block methods.

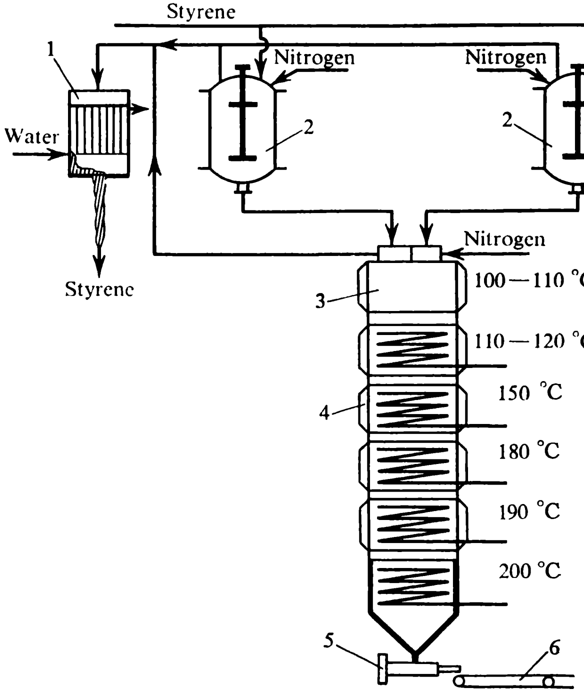
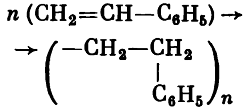


Fig. 97. Diagram for manufacturing polystyrene

1—cooler; *2*—reactors; *3*—polymerization column; *4*—steam jacket; *5*—screw extruder; *6*—roller table

TABLE 29. **Preparation of Polystyrene**

Process	Operation	Apparatus employed
Preparation of polystyrene	Beginning of polymerization of styrene  $n\,(CH_2{=}CH{-}C_6H_5) \rightarrow \rightarrow \left(\begin{array}{l} -CH_2-CH_2 \\ \qquad\quad | \\ \qquad\quad C_6H_5 \end{array}\right)_n$ Completion of polymerization of styrene by heating Feed for processing purposes	Styrene ↓ Reactors with stirrers ↓ Polymerization column ↓ Screw extruder ↓
Processing of polystyrene	Cooling and solidification of polystyrene	Roller table ↓ Block-polymerized polystyrene

The continuous bulk polymerization, as shown in Fig. 97 and Table 29, produces **block polystyrene.** The purified polystyrene is fed to reactors *2* with agitators. These reactors accommodate coiled pipes (not shown in the figure) which carry hot water. Polymerization of styrene occurs in the reactor at a temperature of about 80 °C. From the reactors a liquid mixture of polystyrene and unreacted styrene is admitted to the top of polymerization column *3* for final polymerization, which is carried out in a nitrogen atmosphere.

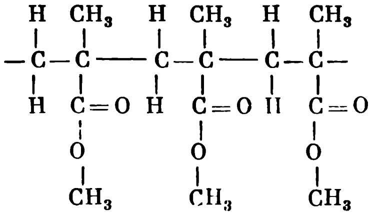
The column consists of six sections, and a strictly predetermined temperature from 100 to 200 °C is maintained in each section. This can be accomplished by heating with steam fed to steam jacket *4*, and by electric heating of the bottom of column *3*. As the styrene moves upwards in the column, its polymerization is completed. The styrene is partially evaporated, its vapours are admitted to cooler *1* where it is condensed and recycled. The molten polystyrene flowing out of the column enters screw extruder *5* which is heated, and then it flows as a continuous viscous stream onto roller table *6* cooled with water or air. There, the polystyrene solidifies, and, after cooling, is transferred for processing. The reactors and the polymerization column are manufactured from aluminium or enamelled steel.

Emulsion polymerization of polystyrene yields emulsion-polymerized polystyrene.

Block-polymerized polystyrene is widely employed in radio engineering, electronics, and other industries as electric-insulating material. It is used to manufacture machine components, facing stabs, films, and domestic appliances.

Emulsion-polymerized polystyrene is a white powder used not only for manufacturing various articles, but also for making foamed plastics.

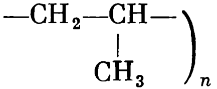
The Manufacture of Polyacrylates. Polyacrylates are products of polymerization of derivatives of acrylic acid, $CH_2{=}CH{-}COOH$. Polymethyl methacrylate—the product of polymerization of methyl methacrylate, $CH_2{=}{=}CCH_3COOCH_3$—has found the widest applications:

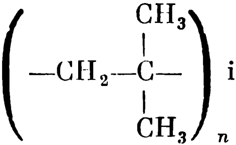


$$\begin{array}{cccccc} \mathrm{H} & \mathrm{CH_3} & \mathrm{H} & \mathrm{CH_3} & \mathrm{H} & \mathrm{CH_3} \\ | & | & | & | & | & | \\ -\mathrm{C} - & \mathrm{C} - & \mathrm{C} - & \mathrm{C} - & \mathrm{C} - & \mathrm{C} - \\ | & | & | & | & | & | \\ \mathrm{H} & \mathrm{C{=}O} & \mathrm{H} & \mathrm{C{=}O} & \mathrm{H} & \mathrm{C{=}O} \\ & | & & | & & | \\ & \mathrm{O} & & \mathrm{O} & & \mathrm{O} \\ & | & & | & & | \\ & \mathrm{CH_3} & & \mathrm{CH_3} & & \mathrm{CH_3} \end{array}$$

Emulsion, block, and varnish methods are used to produce a polymer with the formula $(-CH_2-CCH_3COOCH_3-)_n$ i.e. polymethyl methacrylate. It is highly transparent and is therefore called **plexiglass**. Plexiglass is a very hard readily mouldable material. It is oil- and petrol-resistant, can be readily machined and coloured. Plexiglass is employed for glazing airplanes and automobiles and in the manufacture of chemical equipment. Plexiglass is also used in radio engineering and in the manufacture of domestic appliances. The ability of plexiglass to pass ultraviolet rays made it useful for glazing hothouses.

Polypropylene, polyisobutylene and polyformaldehyde are derived from polymerization resins.

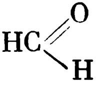
Polypropylene  $\left(\begin{array}{c}-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\end{array}\right)_n$ has high mechanical strength and a higher softening temperature than polyethylene. It is resistant to solutions of acids, alkalis, salts, and organic solvents. Pipes, containers, various components and fibres are manufactured from polypropylene.

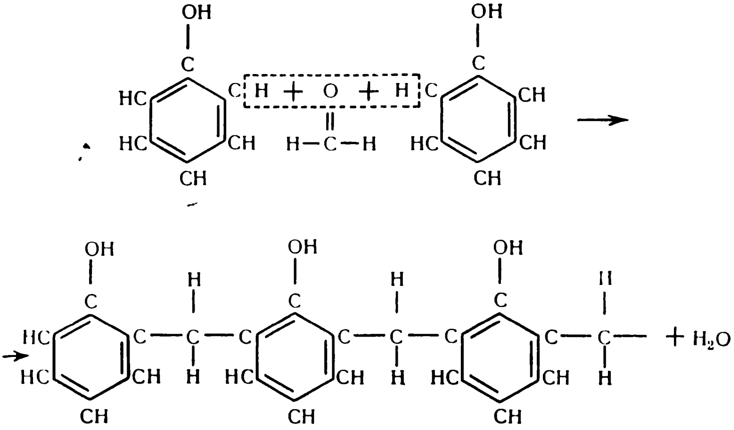
Polyisobutylene  $\left(\begin{array}{c}-CH_2-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-\end{array}\right)_n$ is a rubber-like mass which is readily miscible with fillers, such as soot and graphite. It is chemically stable and plastic, and is therefore used for protecting apparatus from corrosion.

Polyformaldehyde $(-CH_2-O-)_n$ is insoluble at low temperatures in conventional solvents. It is resistant to many chemical media, mildew, insects and has high dielectric and mechanical properties. The polymer is rigid, hard, and retains its properties even when heated to 120 °C; used to manufacture gears, plain bearing inserts, pipes, and sheets.

16.2 Polycondensation Resin-based Plastics

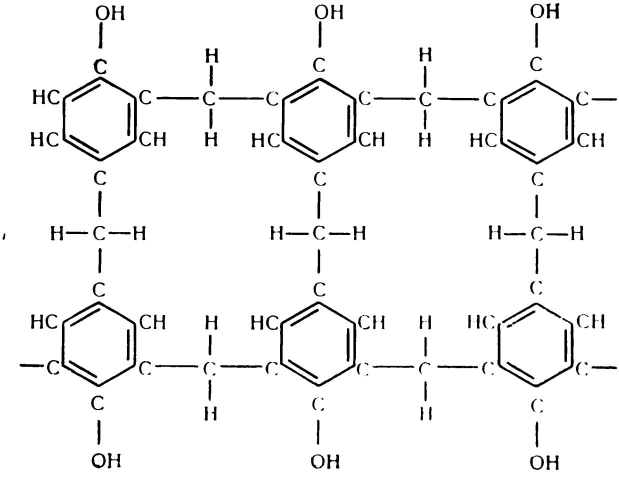
Thermosetting polycondensation resins, such as a phenol-formaldehyde, carbamide, and the like, are used as a binding agent in the composition of thermosetting plastics and play no less important role than thermoplastics.

Phenol-formaldehyde resins and plastics based on them are produced by phenol, C_6H_5OH, condensation with formaldehyde,  $HC\begin{array}{l}\nearrow O\\ \searrow H\end{array}$. Mixing of aqueous formaldehyde (formalin) with large amounts of phenol, followed by the addition of an acid (catalyst) and heating initiate the following reaction:



This reaction yields *novolak resin*. This resin is thermoplastic, since its molecules have a linear structure.

Mixing large amounts of formalin with phenol in the presence of an alkali (catalyst) and heating will produce *resol resin*.



The molecules of this resin have a spatial structure and the resin is therefore thermosetting.

The apparatus employed for manufacturing novolak and resol resins differ slightly from each other (Fig. 98). Reactor *1* accommodated with a stirrer is charged with phenol, formalin, and a catalyst. The mixture is stirred and heated to 70 or 75 °C by feeding steam to the reactor jacket. Then heating is discontinued. Due to the reaction heat, the temperature is raised to 90 °C. To prevent any further temperature rise, cold water is fed to the reactor jacket. After leaving reactor *1*, water vapour is cooled in cooler-condenser *2*, and the condensate is returned to the reactor. A mixture is formed in the reactor. It includes water, unreacted phenol and formaldehyde, and the resulting resin. To obtain dry phenol-formaldehyde resin, rarefaction is created in the reactor and steam is fed to the reactor jacket for heating. The condensate formed in cooler-condenser *2* is collected in vacuum receiver *3*. The resin is allowed to leave the reactor

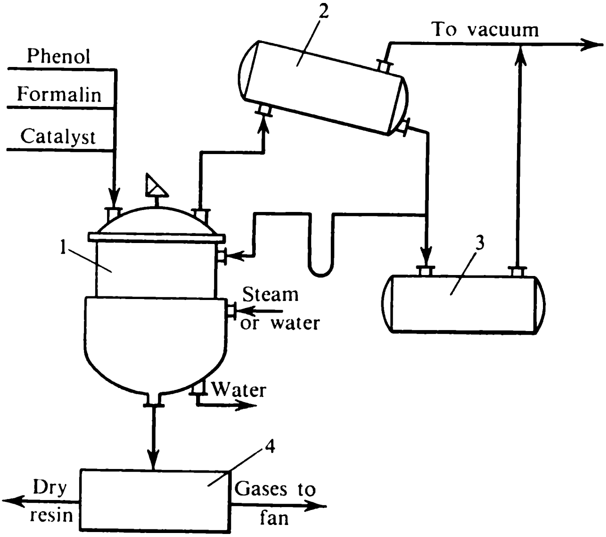


Fig. 98. Diagram for manufacturing resin

1—reactor; *2*—cooler-condenser; *3*—vacuum receiver; *4*—pan onto pan *4* where it is cooled and then sent to the storage site.

The batch process for producing phenol-formaldehyde resin is shown in Fig. 98. At the present time, the continuous polycondensation of phenol with formaldehyde has been put into practice. It is carried out identically with the continuous process for producing styrene.

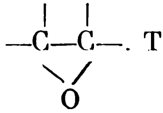
Phenol-formaldehyde resins are used to produce cast plastics without fillers or with fillers to produce powdery and fibrous substances. They are used as a binding agent in laminated plastics, as adhesives and varnishes, and in the manufacture of cellular plastics. The fillers used include wood meal, asbestos, talc, kaolin, magnesium, and the like. When the filler is asbestos, faolite is produced which is a chemically stable material used in the manufacture of chemical equipment.

Phenol-formaldehyde resin-based plastics have high strength, chemical stability and electric-insulating properties. They are used to manufacture components of radio equipment, parts which are operational at elevated temperatures and in aggressive media.

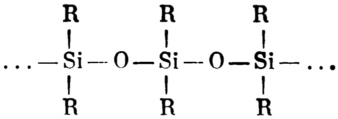
Aminoplasts are produced by condensing carbamide (urea), $(NH_2)_2CO$, with formaldehyde. Aminoplasts are thermosetting. They are used with various fillers to manufacture consumer goods, electric-insulating articles, and building and facing materials.

Polyether resins are produced by polycondensing polybasic acids with polyhydric alcohols. They are used for manufacturing electric-insulating compositions, varnishes, and enamels.

Polycarbonates—polyesters of carbonic acid—are produced, for example, from phosgene, $COCl_2$, and diphenyllpropane, $HOC_6H_4—C(CH_3)_2—C_6H_4OH$ in an alkaline medium. The resulting polycarbonate—a solid transparent ubstance—is employed for manufacturing electric-insulating parts, radio components, and heating devices.

Epoxy resins are based on compounds containing an epoxide (oxide) group  $-\underset{\mathrm{O}}{\underbrace{\overset{|}{\mathrm{C}}-\overset{|}{\mathrm{C}}}}-$. They are used to manufacture components and units of electric devices, and also for making coatings and adhesives.

Organosilicon compounds—polyorganosiloxanes—are high-molecular compounds whose chain structure is formed by silicon and oxygen, silicon is bonded with organic radicals:



$$\ldots-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}}-O-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}}-O-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}}-\ldots$$

where R is CH_3, C_2H_5, etc. Organosilicon compounds are produced as liquids of varying viscosity, and as solids with linear and three-dimensional macromolecules. They exhibit variety of properties. This can be explained by changing and differing combination of radicals incorporated in their molecules, and also by the size of the resulting macromolecules.

Organosilicon compounds can withstand considerable heating. They can be used for a prolonged period of time at a temperature of 200 °C or temporarily at a temperature of 500 °C or higher. They are stable in water, and change their viscosity only slightly during temperature variations. Many organosilicon compounds have excellent dielectric properties; they are reliable insulators. This made it possible for them to be used extensively in various industries as lubricating oils, adhesives, varnish coatings, gaskets, and heat-resistant enamels.

Laminated plastics are produced by impregnating fabrics with synthetic resin solutions. Impregnation of cotton fabrics with a phenol-formaldehyde resin and subsequent hot pressing produce **fibre laminates** which show improved water resistance and considerable strength. They are used for manufacturing machine components.

Another laminated plastic, **glass fibres**, is stronger than fibre laminates. They are manufactured from glass cloth impregnated with phenol-formaldehyde, epoxy and organosilicon resins. Glass fibres produced from glass cloths impregnated with organosilicon compounds present considerable interest. They can withstand high temperatures without any change in their external shape. Glass fibres are useful in the automobile and airplane making industries and in the manufacture of machine and boat components. They are also used as electric-insulating materials or the like.

16.3 Esters of Cellulose and Ester-based Plastics

Cellulose, $(C_6H_{10}O_5)_n$, is a natural colourless infusible and insoluble substance found in the cells of wood, cotton and other plants.

Cellulose is a high-molecular alcohol: its molecules contain a hydroxyl group. Cellulose reacts with various substances; its reaction with acids yields esters of cellulose. Treating it with a mixture of nitric and sulphuric acids causes the nitric acid to combine with cellulose molecules to form the ester of nitric acid and cellulose which is referred to as **nitrocellulose**. Cellulose and acetic acid or its anhydride (acetanhydride) produce **acetylcellulose**. Plastics cannot be obtained from cellulose esters, as they are inadequately thermoplastic. To make them plastic, they are mixed with plasticizers, such as camphor.

After dissolving them in an alcoholic solution of camphor, and subsequently removing them from the alcohol, nitrocellulose forms a plastic—**celluloid**. When heated, celluloid becomes plastic and can easily be treated mechanically or dyed. Celluloid articles are light and have a fine external appearance. Haberdashery, toys or the like can be manufactured from celluloid. Acetylcellulose is employed for manufacturing plastics and silk, and for making varnishes, safety cine- and photographic films.

16.4 Manufacture of Articles from Plastics

Methods for processing plastics are based on polymer ability to acquire plasticity and fluidity when they are treated with temperature and pressure, and then to retain the shape that they have been given in ordinary conditions.

Depending on their behaviour during heating, plastics are subdivided into thermosetting and thermoplastic ones. Therefore, their processing methods are determined by their belonging to one of these groups. For example, when processing thermoplastics, the material remains fusible in the manufactured article and can be reprocessed, unlike thermosetting materials which can chemically change due to the effect of temperature and pressure during the processing operation. These reactions render the manufactured article infusible and insoluble.

The basic methods for processing plastics into useful articles are as follows: compression moulding, injection moulding, extrusion, sheet forming, the manufacture by rolling, and also welding and mechanical treatment.

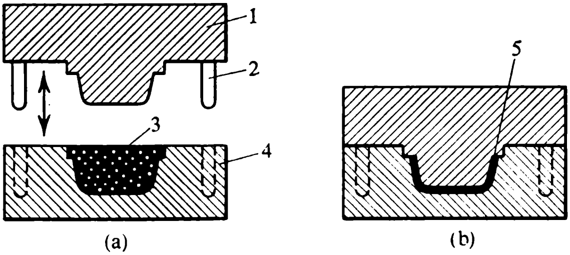


Fig. 99. Diagram of compression moulding

(*a*) mould open; (*b*) mould closed
1—male die; *2*—guide rods; *3*—polymer; *4*—female die; *5*—article

Compression moulding (Fig. 99) is mostly employed to process thermosetting resins. If this method is used, polymer *3* (in powdery or tablet form) is placed in the cavity of the lower portion of female mould die *4*, and heated by steam or electricity. The material becomes molten and, when pressed by male mould *1*, fills up its working portion. After cooling, the mould is opened and the article is taken out.

Compression moulding is seldom employed with thermoplastic resins, the resulting article must be kept in the mould until completely cooled. This increases the duration of the process.

Injection moulding is employed to process thermoplastic materials, such as polyethylene, polystyrene or the like. Powdery or granular material *5* (Fig. 100) is fed to filling funnel *4* from which it is sent to chamber *3* which is being heated. The material remains plastic in this chamber and acquires the ability to flow under pressure. Plunger *6* set in rotation by an electric motor operates in this chamber. As the plunger moves forward, the softened material is admitted through a nozzle to a cold mould where it solidifies. After extrusion of the material, the plunger moves back and

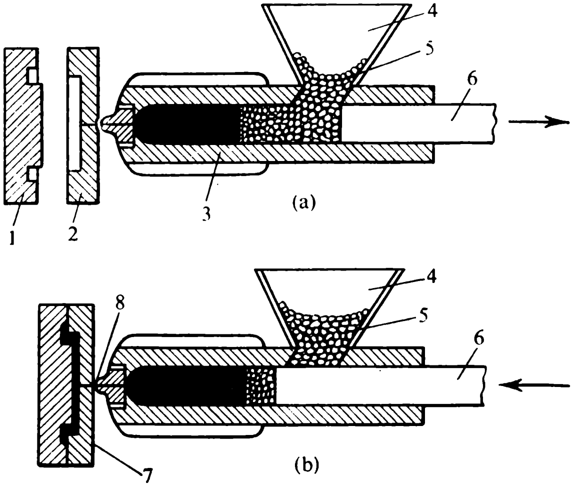


Fig. 100. Injection-moulding machine

(*a*) mould open; (*b*) mould closed
1—movable mould plate; *2*—fixed female plate; *3*—chamber being heated; *4*—funnel; *5*—material; *6*—plunger; *7*—article; *8*—nozzle

a fresh portion of powdery material is admitted to the chamber from the filling funnel. Then, the plunger moves forward, and so on. Such a method allows all the operations to be performed without cooling the mould.

The extrusion method allows sheets, films, rods, pipes or the like to be manufactured from polymeric materials. These articles can be produced only by a continuous moulding process. This is accomplished by using special machines, **extruders** (Fig. 101). Extruders are comprised of filling funnel *2* through which powdery material *3* is fed, cylindrical chamber *4* and screw conveyer *5*, which closely adjoins the chamber walls, rotates inside this chamber.

As screw conveyer *5* rotates, the material is first admitted to the chamber zone being heated, where it becomes plastic, and then extruded through extruder die *1*. The shape of the extruder die determines the profile of the resulting article. As the article leaves the extruder die, it cools rapidly.

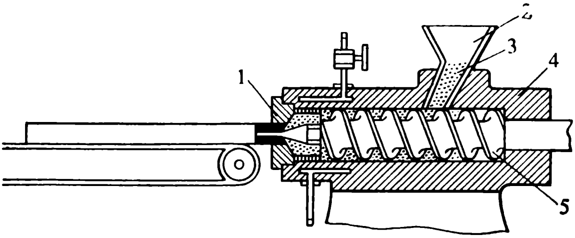


Fig. 101. Extruder

1—extrusion die; *2*—funnel; *3*—material; *4*—chamber; *5*—screw conveyer

This method makes it possible to apply plastics onto wire or other articles.

Sheet forming is employed in processing thermoplastic materials and manufacturing from them articles of complicated shape that have a large surface and small wall thickness.

The diagram of sheet forming is shown in Fig. 102. A blank is prepared from sheet *1*, which is heated to the high-elastic state, it is then secured to female mould die *3* of the stamp installed on the fixed plate of the press. The blank is then pressed by male die *2*. The blank is kept between the female die and the male die until it gets cool and the shape becomes fixed.

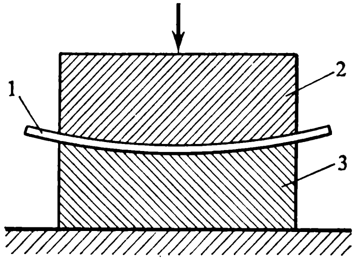


Fig. 102. Diagram of sheet forming

1—sheet material; *2*—male die; *3*—female die

Welding of plastic materials is employed to join components manufactured from thermoplastic materials. Heating the components to be joined is done by gas heat carriers, friction heat, high-frequency currents, or ultrasound. The choice of the welding method (heating temperature and residence time) depends on the properties of the material to be welded, the shape, purpose, and operating conditions of the article.

All types of plastics are subjected to **mechanical treatment.** The latter is accomplished on conventional wood-processing, metal-cutting, special machine tools, or manually.

REVIEW QUESTIONS

1. What materials are called plastics?
2. What is the composition of simple and filled plastics?
3. Draw diagrams for the polymerization of ethylene and styrene.
4. Write the formulas of the polymerization resins and name the fields of application of polymerization resin-based plastics.
5. Write the equations of reactions that produce novolak and resol resins. What are their properties?
6. Depict the diagram of the process for producing phenol-formaldehyde resins.
7. What polycondensation resins do you know and what are their properties?
8. What compounds are referred to as organosilicon compounds? Give their general formula.
9. What cellulose esters are used for manufacturing plastics and films?
10. Use Figs. 99-102 to explain the processes for manufacturing articles from plastics.

Chapter 17

MANUFACTURE OF CHEMICAL FIBRES

Fibres are fine, flexible, strong, thread-like bodies that have a very small cross section.

From ancient times people have worn clothes made from natural textile fibres, such as wool, silk, flax, and cotton. The assortment of textile materials had become considerably diversified when chemical processes for producing fibres were devised three or four decades ago. These fibres came to be known as chemical ones. There exist two types of chemical fibres, artificial and synthetic ones.

Artificial fibres are manufactured from natural high-molecular compounds such as cellulose, casein, or the like, and **synthetic fibres** are manufactured from high-molecular compounds synthesized from monomers.

The development of processes for manufacturing chemical fibres has opened up boundless opportunities for making fibres which are superior to natural fibres in their properties and meet various requirements. These fibres are stronger and lighter than natural ones, they are neither water wettable nor are affected by rot or mildew, and some of these fibres are chemically stable.

The manufacture of chemical fibres allows employing mechanization and automation of the technological processes. The cost of chemical fibres is generally lower than that of natural ones.

17.1 Processes for Manufacturing Fibres

There is much common between the methods for making various fibres. The process is made up of four stages: (1) preparation of the starting material; (2) preparation of a spinning paste; (3) fibre spinning; and (4) fibre finishing.

Preparation of the starting material. The starting material must be a polymer with a strict linear or slightly branched structure.

Preparation of a spinning paste for fibre spinning varies with the starting material. To manufacture artificial fibres based on cellulose esters, they are dissolved in a 5 or 6% sodium hydroxide solution, and a spinning solution is thus formed. The spinning paste for manufacturing fibres is prepared by dissolving or melting the polymer.

Fibre spinning is accomplished by stretching a filament from a polymer solution or melt. To this end, the solution or melt is forced through very small holes—spinnerets (Fig. 103). Fine streams of the solution or melt flowing through the spinneret holes are treated with chemical reagents or cooled with the result that they solidify and are transformed into filaments.

Spinnerets are installed on a spinning machine. Each machine is provided with 60 to 100 spinnerets.

There are two processes for fibre spinning—wet and dry.

The *wet process* is carried out when solution spinning is employed (Fig. 104). The spinning solution fed by spinning pump *1* passes through filter *2*, glass tube *3*, is forced through the holes of spinneret *5*, and is then directed to the solution in settling bath *6*. Forced through the spinnerets, fine streams of the spinning solution react with the solution in settling bath *6* to form filaments which are wound onto bobbin *4*. The wet process is used to manufacture artificial fibres, such as viscose and cuprammonium, and sometimes synthetic fibres.

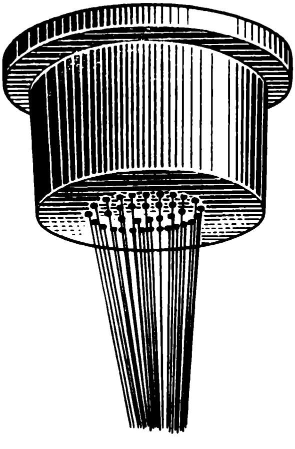


Fig. 103. Spinneret

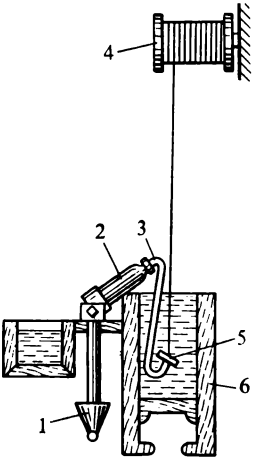


Fig. 104. Polymer solution spinning

1—pump; *2*—filter; *3*—glass tube; *4*—bobbin; *5*—spinneret; *6*—settling bath

The *dry process* is carried out when a polymer solution or melt spinning is employed. When the dry spinning process is carried out (Fig. 105), the heated polymer solution passes through spinning head *1* and spinneret *2* and is admitted in the form of fine streams to spinning machine shaft *3* into which heated air is supplied. The shaft is heated externally with hot water to maintain a temperature of about 80 °C in the shaft. The solvent evaporates at this temperature and fine streams of the spinning solution solidify to form bundle *4* of fibres that are joined together in the bottom of the shaft to form filament *5*, and are wound onto bobbin *6*. The dry process is carried out to manufacture artificial

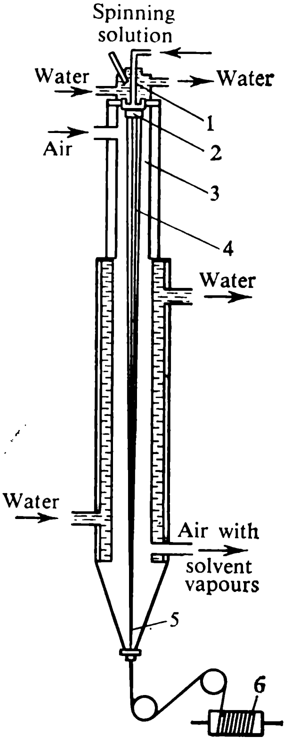


Fig. 105. Dry polymer solution or melt spinning

1—spinning head; *2*—spinneret; *3*—spinning machine shaft; *4*—bunch of fibres; *5*—filament; *6*—bobbin

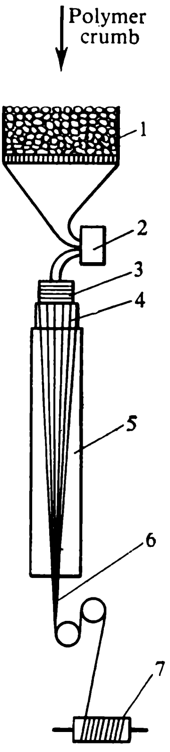


Fig. 106. Melt spinning

1—grid; *2*—pump; *3*—spinneret; *4*—buch of fibres; *5*—spinning machine shaft; *6*—filament; *7*—bobbin fibres, such as acetate rayon, and also some synthetic fibres. •

When solution spinning is used (Fig. 106), resin crumb is fed to grid *1* which is heated, where it becomes molten. The melt is then forced through spinneret *3* by pump *2*. Bunch *4* of fibres is admitted to shaft *5* where the bunch is cooled with air. The fibres solidify in shaft *5* to form filament *6* and are wound onto bobbin *7*. The dry process is used for spinning synthetic fibres, such as capron, nylon or the like.

Fibre finishing removes impurities, dries and, if desired, whitens and dyes the fibres. All fibres are generally treated with fat-containing solutions to facilitate their processing during weaving, knitting or other operations.

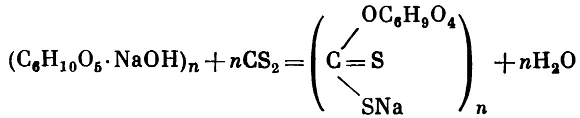
Out of great family of chemical fibres, several types may be singled out. The manufacture of these fibres is expanding most successfully. These are fibres produced from cellulose, polyamide, polyesters, and polyacrylonitrile. It appears that they will also find preferable uses by the end of this century.

17.2 Manufacture of Artificial Fibres

The Manufacture of Viscose Fibres. Cellulose is used as the raw material for this process. The first stage of the process is the preparation of a spinning solution. The cellulose is primarily treated with a 18 to 20% sodium hydroxide solution. In this case, the reaction produces alkali cellulose:

$$\underset{\text{cellulose}}{(C_6H_{10}O_5)_n} + nNaOH = \underset{\text{alkali cellulose}}{(C_6H_{10}O_5 \cdot NaOH)_n}$$

The alkali cellulose is forced out from the alkaline solution, kept for 12 to 24 hours at 20 to 22 °C and then treated with carbon disulphide CS_2. Here, cellulose xanthate is produced:



$$(C_6H_{10}O_5 \cdot NaOH)_n + nCS_2 = \underset{\text{cellulose xanthate}}{\left(C \begin{matrix} \diagup OC_6H_9O_4 \\ = S \\ \diagdown SNa \end{matrix} \right)_n} + nH_2O$$

cellulose xanthate

The cellulose xanthate is dissolved in a 4 to 7% sodium hydroxide solution at 25 to 30 °C to form a spinning solution from which impurities are removed by centrifuging. The solution is kept for some time and transferred for spinning viscose fibres.

Viscose fibre spinning is accomplished by the wet process. The spinning solution passes through the holes of the spinneret immersed in settling baths containing an aqueous solution of sulphuric acid, sodium sulphate, and zinc sulphate. Fine streams of the cellulose xanthate are admitted from the spinneret holes into the bath. In this case, the cellulose xanthate coagulates and decomposes to form viscose fibres. In the bath or after the bath, the fibres are stretched and wound onto bobbins.

Viscose fibres are resistant to the action of organic solvents and are maintained in the range of 100 to 120 °C. Viscose fibres are disadvantageous in that they lose strength considerably in the wet state and show low resistance to alkalis.

The Manufacture of Acetate Fibres. Acetate fibre is spun by the dry process from acetyl cellulose solutions in a mixture of acetone and alcohol. The solution is forced through the spinneret holes into the shaft of the spinning machine where air is supplied at a temperature of 55 to 70 °C.

Acetate exhibits great elasticity and loses strength in the wet state to a smaller extent than viscose fibres. Acetate is an excellent electric insulator.

17.3 Manufacture of Synthetic Fibres

Synthetic fibres have a great variety of properties. Some are readily soluble in water, the others neither absorb moisture nor swell. They are very strong and chemically stable and are not affected by microorganisms.

At the present time the number of synthetic fibres manufactured industrially is steadily growing. A large group of synthetic fibres includes **polyamide fibres**, such as capron, nylon, and enanth.

Capron fibre is produced from capron resin which is itself derived from caprolactam. Polymerization, i.e. transformation of caprolactam into resin, occurs in an autoclave at a temperature of 250 °C and at a pressure of about 15 kgf/cm^2 in a nitrogen atmosphere. The molten resin is forced out of the autoclave by nitrogen in the form of a narrow ribbon which then solidifies and is crushed. The crumb resulting from crushing is washed with water, dried, and is directed for spinning purposes. Capron is produced by the melt spinning process. The fibre is extended, washed and dried.

Capron fibres show high resistance to attrition and are strong, elastic, and resistant to alkalis. Fabrics for clothes, industrial fabrics (filter cloth and cord fabric, etc.), textiles, electroinsulating materials, or the like are manufactured from capron fibres.

Nylon fibre is produced from nylon resin synthesized by polycondensation of adipic acid $HOOC—(CH_2)_6—COOH$ with hexamethylene diamine $H_2N(CH_2)_6NH_2$. Nylon fibre is produced by the dry melt spinning process. Nylon differs from capron by its higher melting temperature. Physicochemical parameters and the field of nylon application are similar to those of capron.

Enanth fibre is produced from enanth resin synthesized by polycondensation of aminoenanthic acid $H_2N(CH_2)_6COOH$. The fibre is produced by the dry melt spinning process. Enanth fibre is not inferior to capron, and is superior to it in some respects. It shows higher light- and thermal stability than capron fibre. Its use is similar to that of capron fibre.

Lavsan fibre is a polyester fibre. It is manufactured from lavsan resin produced by polycondensation of dimethyl ester of terephthalic acid $H_3COOC(C_6H_4)COOCH_3$ with ethylene glycol $HOCH_2CH_2OH$.

Lavsan fibre is produced by the dry melt spinning process. This fibre is similar to that of wool with respect to heat conduction; it is not affected by moisture and shows high stretch resistance. It is superior to most synthetic fibres with respect to thermal stability.

Lavsan fibre is used for manufacturing fabrics, textiles, filters, cord, and electroinsulating materials, conveyer belts, and the like.

Chlorin fibre, polyvinyl chloride fibre, is produced from chlorin resin which is chlorinated polyvinyl chloride.

This fibre is produced by the dry and wet spinning processes. Dry spinning is effected from a resin solution in a mixture of acetone and benzene, and wet spinning from a solution in dimethylformamide and tetrahydrofuran. To make the solutions less viscous, they are forced through spinnerets at elevated temperatures. Chlorin fibre has high chemical stability and is used for manufacturing filter cloths and other materials for the chemical industry, fishing tackles or the like.

Nitron fibre, polyacrylic fibre, is spun from polymers produced on the basis of acrylonitrile CH_2—CHCN or its copolymers. The fibre is produced by the dry and wet processes.

Nitron is resistant to oxidizers, heat (up to 120-130 °C), and light. It does not lose strength in a humid medium, is not affected by rot, but has low hygroscopicity and is relatively poorly colourable. Yarn from polyacrylic fibres is used for making textiles, filler cloths, upholstery materials and other fabrics, sail cloths, ropes, and so on.

The remarkable properties of chemical fibres and the possibility of producing fibres with predetermined properties were responsible for their manufacture on a great scale. In many cases, natural fibres were replaced by chemical ones, such as cotton, flax, silk, wool, or the like. The rate of growth of the manufacture of chemical fibres is ahead of the manufacture of natural fibres.

REVIEW QUESTIONS

1. What fibres are called artificial and synthetic?
2. What raw materials are used for manufacturing artificial and synthetic fibres?
3. What is meant by dry and wet spinning?
4. What is the essence of the process for producing viscose fibre?
5. What synthetic fibres do you know? What are their properties?

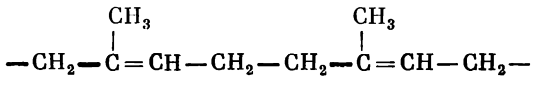
Chapter 18

THE TECHNOLOGY OF RUBBER AND VULCANIZED RUBBER

Rubber is an elastic high-molecular compound which changes shape due to the effect of external forces, and assumes the original shape if these forces are no longer applied. The ability of rubber to change shape is explained by the fact that macromolecules of rubber exist in a rolled-up state, in the form of spirals. When stretched, they become straightened to a considerable extent, and after the stretch load is removed they roll up again spontaneously.

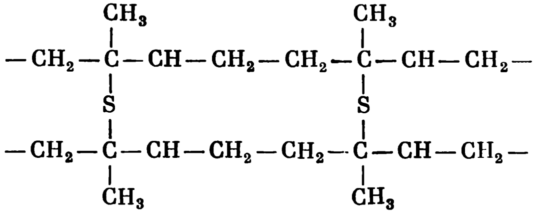
Rubber has been known for a long time. Its remarkable properties, ability to be considerably elongated when stretched and be contracted when compressed, and its elasticity and flexibility, could not be duplicated for a long time. This is explained by the fact that rubber articles lost rapidly the shape and most of their valuable properties, too. Only after a process for vulcanizing rubbers was devised which allowed producing vulcanized rubber from rubber, were the elasticity and resilience of rubbers combined with excellent mechanical strength and resistance to heat and cold. These products became widely used in many industries.

What is the essence of the vulcanization process? As has been indicated, the rubber molecules are spirals that are capable of being extended or compressed by external forces. At the same time, the forces interacting between individual polymer chains of rubber are very weak and the molecules are capable of moving relative to each other, especially when heated. Vulcanization binds the molecules together and eliminates their mobility. Sulphur is a vulcanizing agent. It joins the chains of the micromolecules of rubber to form "bridges" between them. For example, vulcanization of rubber with the linear molecular structure:



$$-CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2-CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2-$$

yields cross-linked macromolecules with sulphur "bridges" between the macromolecules:



$$\begin{array}{ccccc} & CH_3 & & CH_3 & \\ & | & & | & \\ -CH_2- & C & -CH-CH_2-CH_2- & C & -CH-CH_2- \\ & | & & | & \\ & S & & S & \\ & | & & | & \\ -CH_2- & C & -CH-CH_2-CH_2- & C & -CH-CH_2- \\ & | & & | & \\ & CH_3 & & CH_3 & \end{array}$$

In combination with fillers, such as soot, this rubber is known as *vulcanized rubber*; it shows mechanical strength, resistance to heat, and also to solvents and other reagents.

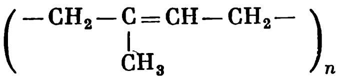
Vulcanized rubber is widely used to manufacture auto and aircraft tyres, drive belts, conveyer belts, flexible hoses, machine components, electroinsulating materials, rubber-coated fabrics, footwear, articles of sanitation and hygiene.

Rubbers are subdivided into *natural* and *synthetic* rubber.

18.1 Natural Rubber

Natural rubber (NR) is a naturally occurring high-molecular substance of plant origin. It is derived from a great number of plants—rubber-yielding plants, among which Brazilian Hevea plays the basic industrial role. At the present time, natural rubber is mostly produced on plantations located on South-East Asia islands.

Natural rubber is extracted by making a cutting on the bark of a Hevea tree, a milky sap—latex—flows out of the cutting. It contains 20 to 35 per cent of a rubber substance. This substance is a high-molecular polymer of isoprene, $CH_2{=}\underset{\substack{|\\ CH_3}}{C}{-}CH{=}CH_2$. Thus, the macromolecule of natural rubber is composed of these elementary links:



$$\left(\begin{array}{c} -CH_2-\underset{\substack{|\\ CH_3}}{C}=CH-CH_2- \end{array}\right)_n$$

To extract the rubber, acetic or formic acid is added to the latex. Here, the particles of rubber (globules) roll up and *coagulation* occurs. The rubber is then recovered in the form of a porous voluminous blob. The rubber is filtered, washed with water, and passed through corrugated rolls. Vulcanized rubber processed from natural rubber possesses high mechanical strength and elasticity within a wide range of temperatures.

18.2 Synthetic Rubbers

The ever growing demand for rubber and dependence of many countries on those producing natural rubber posed a problem for scientists throughout the world working at the problem of producing *synthetic rubber* (SR). Attempts to synthesize rubber had for a long time ended in failure.

In 1928, S. Lebedev obtained butadiene rubber by polymerization of butadiene (divinyl). A plant to manufacture synthetic rubber was commissioned in 1932.

As has been noted, *butadiene rubber* (SRB) is produced by butadiene polymerization.

At the beginning of rubber production butadiene, $CH_2{=}CH{-}CH{=}CH_2$, was derived from ethanol which in turn was obtained from food products, such as grain, potato or the like. At the present time, ethanol is synthesized from ethylene.

Butadiene production by dehydrogenation of butane which is contained, as well as ethylene, in the petroleum and natural gas processed products is of considerable interest. Thus, petroleum and natural gases are the basic raw materials in the manufacture of SRB.

Butadiene rubber is produced in a batch autoclave (Fig. 107) closed with cover *3*, where liquid or gaseous butadiene is fed through pipe connection *2*. Bulk polymerization occurs at a temperature of 30 to 40 °C and at a pressure of 9 or 10 kgf/cm^2 with a catalyst, such as metallic sodium rods. At the beginning of the process, steam is fed to jacket *1* of the autoclave to accelerate polymerization, and water is then fed to remove the heat that evolves in the course of the reaction. On completion of the polymerization process, the pressure falls in the autoclave, the unreacted butadiene and other gaseous products are removed. Rubber is discharged in the form of a block from the apparatus in a nitrogen atmosphere.

Vulcanized rubber manufactured from butadiene rubber is inferior to vulcanized rubber manufactured from natural rubber with respect to strength, elasticity and wear resistance. SRB is used to manufacture auto tyres, footwear, rubberized fabrics, etc.

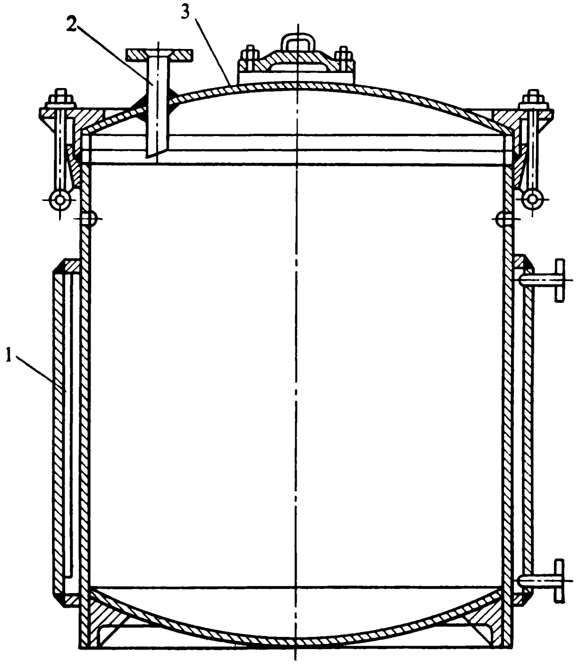
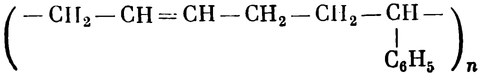


Fig. 107. Autoclave

1—jacket; 2—pipe connection; 3—cover

Butadiene-styrene rubber (SRS, Buna-S, or the like) is produced by copolymerization of butadiene with styrene.

Rubber is composed of macromolecules:

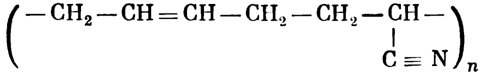


$$\left(-CH_2-CH=CH-CH_2-CH_2-\underset{C_6H_5}{\underset{|}{CH}}- \right)_n$$

Polymerization is carried out by the emulsion method at a temperature of 5 to 50 °C. Butadiene and styrene are first mixed with water and an emulsifier (rosin soap, or the like), and preliminary emulsification is effected. Together with an initiator solution (isopropyl benzene hydroperoxide), the emulsion passes successively through a battery of polymerizers consisting of 12 apparatus. The polymerizer is a 12 to 20 m^3 capacity steel apparatus provided with agitators and lined from inside. As the emulsion passes the battery of polymerizers, about 60 per cent of the initial monomers are transformed into polymers. Thus, a latex is produced from which the unreacted monomers and other impurities are separated. Coagulants (common salt, NaCl, or calcium chloride, $CaCl_2$, sulphuric acid, H_2SO_4, or acetic acid, CH_3COOH) are then added to the latex (coagulants) in whose presence the rubber rolls up, i.e. coagulates. It is separated from the solution, washed, moulded into the form of ribbons and rolled up. To avoid adhesion of the rolled-up rubber, rubber ribbons are powdered with talc.

Butadiene-styrene rubber is used to manufacture tyres and conveyer belts. Some grades of SRS are similar to natural rubber with respect to frost resistance, they are used therefore to manufacture frost-resistant rubber articles.

Butadiene-nitrile rubber (SRN and Buna-N) are copolymers of butadiene and nitrile of acrylic acid $CH_2{=}CHCN$ having the formula:

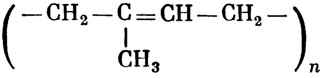


$$\left(-CH_2-CH=CH-CH_2-CH_2-\underset{\displaystyle C\equiv N}{\underset{|}{CH}}- \right)_n$$

Copolymerization occurs in an aqueous emulsion.

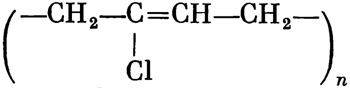
These rubbers show high oil- and petrol resistance. They are used for manufacturing petrol and oil-resistant hoses, gaskets, and other articles which are essential in the petroleum, aircraft, and other industries.

Isoprene rubber (SRN)



$$\left(-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CH_2- \right)_n$$

is produced by polymerization of isoprene at a temperature of 30 to 40 °C in the presence of a catalyst (lithium or complex organometallic compounds). In its structure, synthetic isoprene rubber is similar to natural rubber, therefore the former is very identical to natural rubber in many properties.

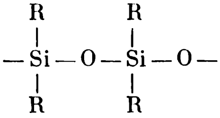
Chloroprene rubber is a polymer of chloroprene. Its formula is  $\left(-CH_2-\underset{Cl}{\underset{|}{C}}=CH-CH_2-\right)_n$. Chloroprene is derived from vinyl acetylene.

Chloroprene polymerization is effected predominantly by emulsion method at a temperature of about 40 °C. Rosin soap and other substances are used as an emulsifier.

Chloroprene rubber is incombustible, resistant to chemical reagents and oils. It has improved heat- and light resistance. Chloroprene rubber is disadvantageous in that it has reduced frost resistance.

Chloroprene rubber cannot be vulcanized by sulphur. Therefore, to convert it to vulcanized rubber so as to produce cross-linked macromolecules, oxides of zinc, mercury, and other metals are used. This rubber is employed in the cable industry as an anticorrosive coating and for making adhesives.

Organosilicon (*siloxane*) *rubbers* are made up of chains typical of organosilicon polymers:



$$-\overset{R}{\underset{R}{\overset{|}{\underset{|}{Si}}}}-O-\overset{R}{\underset{R}{\overset{|}{\underset{|}{Si}}}}-O-$$

Organosilicon rubbers are peculiar in that they show high thermal stability and elasticity. They do not change their properties over the range of temperatures of —60 to +300 °C. They are water resistant, possess electroinsulating properties, are not soluble in oil, petrol, and other solvents. Organosilicon rubbers are used to manufacture heat-resistant gaskets, valves, diaphragms, and also as electroinsulators and other articles operating at high and low temperatures.

Fluorine-containing rubbers are produced from fluoro derivatives of ethylene. Rubbers produced by copolymerization of trifluorochloroethylene $CF_2{=}CFCl$ with vinylidene fluoride $CF_2{=}CH_2$ have found the widest application. These rubbers show a high thermal and chemical stability, and possess high mechanical strength. Due to their high cost, fluorine-containing rubbers are manufactured in limited quantities.

Synthetic latexes normally contain 20 to 33 per cent of rubber. They are used to impregnate tyre cord, gaskets, pipes, and hoses, and for impregnation and coating of paper, in the manufacture of leather, and so on.

18.3 Manufacture of Vulcanized Rubber

The Manufacture of Rubber Articles. The process consists of three basic stages: preparation of the raw rubber mix, moulding the articles, and their vulcanization. In addition to rubber, which is the basic component of the compound, the rubber mix incorporates other organic and inorganic substances known as *ingredients*. The choice and the amount of ingredients in the mix depend on the quality of the initial rubber and the required properties of the resulting rubber articles.

The raw rubber mix generally incorporates the following substances: rubber, vulcanizers (e.g. sulphur), accelerators of vulcanization (diphenyl quanidine), plasticizers (fatty acids, petrolatum, pine resin, paraffin or the like), antiagers (e.g. phenols, phenyl-β-naphthylamine), fillers (such as soot, silicon dioxide SiO_2, zinc white ZnO, and kaolin), and dyes.

The basic condition for manufacturing high-quality rubber articles is to prepare a rubber mix with a uniform distribution of all the ingredients in it. To make the rubber more plastic and more readily miscible with the ingredients, it is heated before processing. In preparing the rubber mix, certain conditions should be observed (temperature, mechanical effects, etc.) at which the macromolecules of the rubber would not change and the mix ingredients would not decompose.

Rubber compounding is conducted most frequently in high-capacity closed mixers. They are a chamber in which two rotors of the shaft or drum of an oval or three-facet form and provided with lugs rotate at different speeds. The chambers and the rotors have a device for cooling to remove the heat evolving during rubber plasticization.

To effect compounding of the rubber mix, rolls are also used (Fig. 108), whose rollers (*1* and *3*) rotate at different speeds. To avoid premature vulcanization, sulphur is added at the end of the compounding. The resulting rubber mix is moulded by passing it through cylindrical rolls in the form of a continuous ribbon of uniform thickness to be further cut into sheets. The moulded sheets of the rubber mix are located and spaced so as to cut parts and blanks for rubber articles. The further processing of parts and blanks into articles depends on their shape, purpose, and operating conditions.

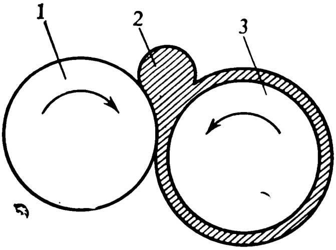


Fig. 108. Rolls
1, *3*—rollers; *2*—rubber mix

Besides, to mould a rubber mix, extrusion machines are used in which the rubber mix is forced through holes of various shapes and cross-sectional size. Rubber tubes and hoses are manufactured in the manner described above.

Vulcanization is the final stage for manufacturing rubber articles. Rubber vulcanization may be effected at ambient temperature (*cold vulcanization*) or by heating (*hot vulcanization*). Cold vulcanization occurs in the presence of 2 or 3% sulphur chloride solutions for 1 to 3 minutes. Cold vulcanization is employed only to manufacture thin-walled articles from a rubber mix. This vulcanization involves solvent losses and hazardous working conditions. Therefore, hot vulcanization at temperatures of 125 to 160 °C using sulphur as a vulcanizing agent is preferred. Hot vulcanization is conducted either in presses or vulcanizing kettles—autoclaves in an atmosphere of hot air or saturated steam.

The classification of vulcanized rubbers. These are subdivided into the following groups:

(1) general-purpose vulcanizer rubbers which are functional at temperatures in the range of —50 °C to +150 °C (tyres, footwear, belts, shock absorbers, etc.);

(2) heat-resistant vulcanizer rubbers employed for pro-

longed use at temperatures higher than 150 °C (components of airplanes, machines, electric motors or the like);

(3) frost-resistant vulcanized rubbers which are functional in the Extreme North, Antarctica, and at high latitudes;

(4) chemically stable vulcanizer rubbers which are resistant to ozone, oxygen, acids, alkalis, salt solutions or the like;

(5) oil-resistant vulcanized rubbers which are resistant to petrol, kerosene, and petroleum;

(6) gas-filled vulcanized rubbers usable as a thermo-insulating material;

(7) vulcanized rubbers which are resistant to the effect of radiation and usable in the manufacture of components of X-ray apparatus or the like;

(8) dielectric vulcanized rubbers employed for insulating cables and for other purposes.

The Development of Rubber and Vulcanized Rubber Production. The amount of rubber and vulcanized rubber produced is determined primarily by the needs of motor transport and the aircraft industry. The requirements for rubber and vulcanized rubber in the other industries, in transport, agriculture, and for every-day purposes is steadily growing. Both the quantity and the assortment of rubbers and vulcanized rubbers which are intended for use in the most diverse fields are expanding.

In 1960 the world's rubber consumption totalled 3.9 million tons, in 1970, 7.8 million tons, and in 1980, about 14 million tons. Despite their valuable properties, natural rubber suffers from some disadvantages (it is not adequately heat resistant, liable to ageing, and shows no oil resistance). As compared with natural rubber, synthetic rubber has the advantage that, depending on the field of application, a suitable material can be obtained. About 12 basic types of synthetic rubbers and at least 500 of various grades have been created in the second half of the 20th century. The share of synthetic rubber is continuously growing in the total volume of production (1% in 1938, 62% in 1970, and 65% in 1980).

The use of new types of raw materials for producing monomers and perfection of methods of their polymerization is one of the problems facing the rubber industry.

REVIEW QUESTIONS

1. What high-molecular compounds are known as rubbers?
2. What is the general structure of rubber macromolecules?
3. What is natural rubber and how is it extracted?
4. What synthetic rubber was first manufactured by the Lebedev method?
5. What rubber is produced by copolymerization of monomers?
6. How is chloroprene manufactured?
7. What is isoprene rubber, and what properties does it possess?
8. What process is called rubber vulcanization and what is the purpose for carrying it out?
9. Name the basic ingredients of a rubber mix.
10. What are the stages in manufacturing rubber articles?

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